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TECHNICAL GAS ANALYSIS

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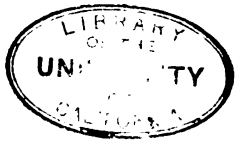
The Industrial Gas Series.

VOLUME I.

TECHNICAL GAS ANALYSIS.

BY

FRANK H. BATES.



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with producer gases; in the case of steam plants where flue gas analysis proves an aid in the maintenance of furnace and boiler efficiency; in connection with gas engine testing, where efficiencies are determined and losses traced by the analysis of the gases admitted and exhausted; and finally in the gas works, where a uniformity of product is a necessary condition to successful manufacture.

The book being written in a plain style, well illustrated by both sketches and examples and with a simple treatment of volume contractions and chemical reactions, make it valuable to the engineer who has no knowledge of chemistry as well as to the expert analyst.

In the preparation of the following chapters the present literature on the subject has been freely consulted, and the author would acknowledge his indebtedness to "Methods of Gas Analysis," by Hempel, in the treatment of the Hempel apparatus, in which the descriptive matter is largely as in the original, but made to conform to the general plan of this work.

FRANK H. BATES.

San Francisco, January 31, 1901.

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CONTENTS.

CHAPTER I.

COLLECTION OF SAMPLES.

PAGE

The plain tube with straight ends to be closed by a blow-pipe 1

The collection tube with glass stop-cocks; Keeping the glass stop-cocks lubricated; Cases for collection tubes; Apparatus for obtaining average samples of a gas, being generated, when the composition varies 2

Suitable piping for conducting gases from furnaces; Porcelain, glass, platinum, lead or rubber tubing; Currents in flue-ways; Getting a sample representing a fair average 5

Collecting mine gases; Packing used in making joints 6

CHAPTER II.

METHODS OF GAS ANALYSIS.

Apparatus to be used for the analysis of furnace or chimney gas, producer gas, illuminating gas; A make-shift apparatus. 7

Analysis with this apparatus 11

CHAPTER III.

THE ORSAT APPARATUS.

Examination of furnace or chimney gases by means of the Orsat apparatus; Description of the Orsat apparatus . . . 17

Manipulation 19

Determination of carbon dioxide 21

Of oxygen 23

Of carbon monoxide; Of nitrogen; Special hints; precautions as to (order of) using the reagents, draining the walls of the burette, time required for an analysis, absorbing capacities of the reagents; limit of error with this apparatus 22

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CHAPTER IV.

THE ELLIOTT APPARATUS.

PAGE

Principle of this apparatus; Description 24
Determination of carbon dioxide 29
Of illuminants; Of oxygen 30
Of carbon monoxide; Treatment of the residue 31
Chemical reactions involved 33
Volume contraction 34
Calculation of the amounts of methane and hydrogen from the combustion with oxygen; Determination of nitrogen by difference; Example of an analysis of coal gas . . . 35
Table of analyses showing range of work to which this apparatus is adapted 38

CHAPTER V.

THE HEMPEL APPARATUS.

When to use this apparatus; Description of the simple gas burette 39
Operation of the gas burette 41
The simple absorption pipette 43
The simple absorption pipette for solid and liquid reagents . 44
The double absorption pipette; The double absorption pipette for solid and liquid reagents 45
The ethylene pipette 48
The explosion pipette 49
The hydrogen generator 50
The explosion pipette with electrodes for the decomposition of water 52
The combustion of methane and hydrogen in a gas mixture without explosion; Operation of the Hempel apparatus . . . 53
Example of an analysis of coal gas 57
Special schemes; The fractional combustion of hydrogen . . . 61
The absorption of oxygen by phosphorus 66
Scheme for the analysis of coal gas by which the traces of carbon monoxide remaining from the cuprous chloride absorption and any ethane present may be determined 67

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CHAPTER VI.

MEASUREMENT OF GASES.

PAGE
Influence of pressure on volume 72
Boyle's law; Example illustrating Boyle's law 75
Influence of temperature on volume 76
Absolute zero; To obtain absolute temperature; Charles' law; Example of Charles' law 77
Vapor tension of liquids 79
Effect of vapor tension on volume 81
Example of combined corrections for pressure, temperature and vapor tension; Measurement of gases over liquids other than water; Measurement of dry gases over mercury; The expansion of mercury 82

CHAPTER VII.

PROPERTIES OF GASES. PREPARATION OF REAGENTS EMPLOYED.

Properties of carbon dioxide; Of ethylene 84
Of oxygen 85
Of carbon monoxide 86
Of nitrogen; Of hydrogen 87
Of methane 88
Preparation of potassium hydroxide; Of sodium hydroxide; Of barium hydroxide; Of bromine water; Of potassium pyrogallate 89
Of cuprous chloride 90
Table I.—Tension of water-vapor in millimeters of mercury for different temperatures, also the weights in grams of the vapor contained in a cubic meter of air when saturated. 91
Table II.—French measure 93
Table III.—Tension of mercury vapor. 93
INDEX 94

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CHAPTER I.—COLLECTION OF SAMPLES.

The method to adopt in collecting a gas sample is dependent upon the conditions under which one is operating. The first point to be observed is to use such means as will give a sample representing the average gas. Oftentimes in the gases to be sampled there exist currents whose composition vary considerably, this being especially true in the case of chemical processes and furnace gases. In such instances some ingenuity must be exercised to meet the special conditions.

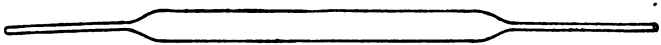

FIGURE 1.

For the retention of a gas sampel, the collection tube shown in Figure 1 will serve. The ends are made quite long and drawn down to about two millimeters ($\frac{1}{16}$ inch) internal diameter. They should be of about 200 cubic centimeters capacity. It will be found very convenient for transportation to have a box, provided with separate

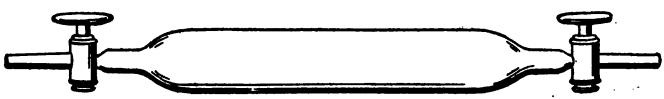

FIGURE 2.

compartments, to hold about a dozen of these tubes. To take a sample it is simply necessary to connect, by a short rubber tube, at one end to the gas supply, allowing the gas to flow through (the gas being under pressure) till certain that all air has been expelled and that only pure

gas remains; then almost stopping the flow to relieve the tube of pressure, seal near the end by holding a lighted candle to it, or by means of an improvised blowpipe made by pointing and nearly closing the end of a glass tube, and then bending near the point, cutting off at a convenient length.

The collection tube will serve for a number of samples before becoming so short as to make it necessary to weld on new ends.

A somewhat handier tube is shown in Figure 2, having glass stop-cocks, which obviates the necessity of sealing by heat. Although there is but little liability to leakage with these tubes when the ground glass stop-cocks fit properly and are kept well greased, yet the writer has made it a practice, when obliged to retain the sample some time before making the analyses, to cover all joints and the open ends with sealing wax, which renders leakage impossible. A case of these collection tubes is shown in Figure 3. Instead of water for the confining liquid, mercury is often used when the previous saturation of the water is inconvenient or for other reasons.

It is sometimes desirable to obtain a sample of a gas passing through a conduit of some kind, which may represent the average gas for a certain period of time. For such purpose the apparatus illustrated by Figure 4 is well suited. The tanks A and B are constructed of galvanized iron, and measure some 12 inches in diameter and 18 inches in length, one being slightly longer than the other. Bottoms and tops of the tanks should be slightly curved downwards and upwards respectively, to render it possible to secure complete drainage. At about the center of both top and bottom is inserted a ¼-inch gas pipe nipple, the joint being strongly soldered, on which are screwed pet-cocks for the tops and pipe connections to the outside for the bottoms, there being a rim sufficient to

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raise the tank above the piping. Pet-cocks are put on the lower pipes at a convenient distance from the side. On the tops there are also auxiliary nipples with pet-cocks attached, to allow of rapid filling.

Operation. The upper (larger) tank is first filled with water and then connected to the gas source by suitable means, while on a shelf below, and with its auxiliary pet-cock connected by rubber tubing to the outlet from

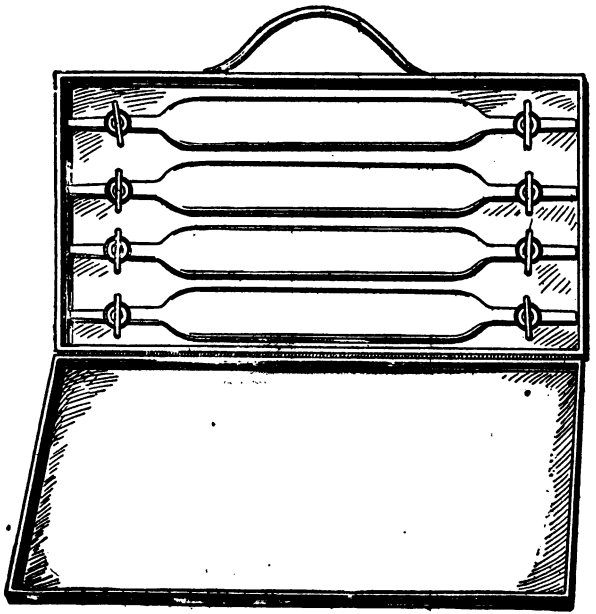

FIGURE 3.

the upper tank, is placed the smaller one. By turning on the globe valve *a* (on the pipe leading to the gas source) and opening pet-cocks *b*, *d*, *e* and *f*, and with pet-cocks *c* and *g* closed, allow the water to run from the tank A into

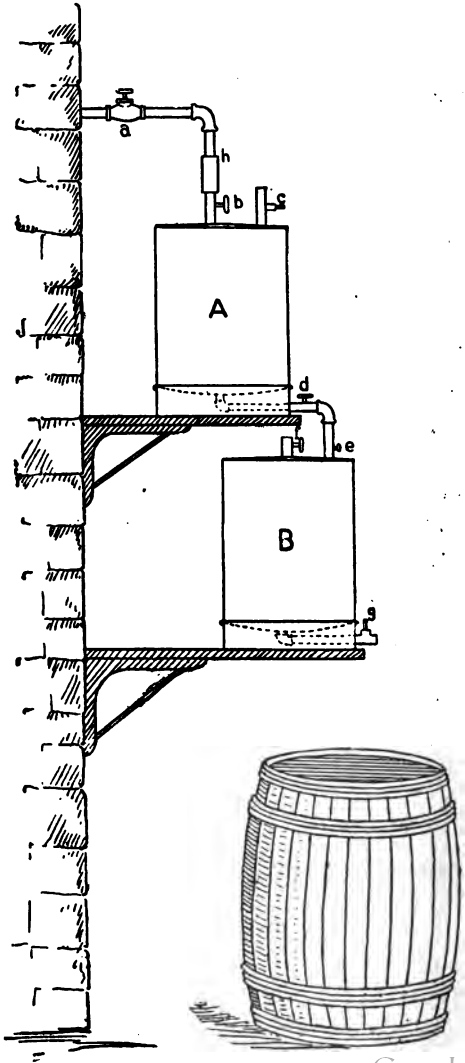

FIGURE 4.

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tank B, displacing the air from the latter and causing it to issue from the open pet-cock *f*. As the water recedes from the tank A, a partial vacuum is created which causes the gas to rush in. The receding water, mingling with the inrushing gas, becomes thoroughly saturated and is used to fill the lower tank B. On the overflow of water from the pet-cock of the tank B, pet-cocks *f* and *e* are closed, and the tank is disconnected from the upper one (which is removed), and connected up to the gas source by attaching the rubber tube *h* to the pet-cock *f*. With a long rubber tube attached to the outlet pet-cock *g*, to serve as a drain to the waste barrel, open the pet-cocks *f* and *g*, causing the water to run from *g* and draw in the gas through *f*. By adjusting these pet-cocks, the time taken to fill the tank may be lengthened or shortened, so that an average sample of a run of a certain duration may be obtained. The previous saturation of the water used prevents the washing out of the soluble constituents of the gas.

The kind of piping to use for running into the furnace or holder will depend upon the temperature and nature of the gases. With a high temperature iron tubes with ample water-jacketing should be employed.* Porcelain, glass or platinum tubes may also be used. Where the gases are strongly acid and the time occupied in making the collection is long, only glass tubes should be employed; they will not be affected by temperatures within 600° C. At temperatures lower than 300° C., lead piping will be found serviceable owing to its great flexibility. Since vulcanized rubber tends to absorb the gases, rubber tubing of any length should be avoided.

In a single flue, way or conduit from which the sample is being drawn, there are often found currents of some

*Iron piping, if raised to a temperature of redness, may alter the gas composition, since the oxygen of the iron oxide (iron rust) will combine with the unsatisfied carbon monoxide to form carbon dioxide

strength and of quite different composition, necessitating, therefore, the use of several branches of piping to penetrate equally all parts and thus afford a fair average. Where the current in the flue way is strong, a suction pump or siphon may be employed to advantage.

For collecting gases from mines, etc., the form of tank shown in Figure 4 may also be used. For this purpose fill with water and place in an upright position where it is desired to sample the gas. By opening both lower and upper pet-cocks cause the gas to replace the water. As soon as the tank empties of water, close all pet-cocks enclosing the sample.

For packing used in making tight joints, asbestos is probably the best, although, under certain conditions, putty, plaster of Paris, or wet waste may be used.

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CHAPTER II.—METHODS OF GAS ANALYSIS.

Apparatus. For furnace and chimney gases, consisting principally of carbon dioxide, carbon monoxide, oxygen and nitrogen, by far the most convenient apparatus is the Orsat, (Fisher's modification) arranged in a portable case.

For furnace or chimney gases, producer gas, and illuminating gas, where great accuracy may be sacrificed to rapidity of operation and convenience, Elliot's latest modification with explosion burette, half size, and arranged in a traveling case, is suitable.

For accurate laboratory analysis, use Hempel's apparatus.

It sometimes happens that one is so situated as to make it desirable to obtain a rough estimate, or an approximation, of the constituents of a gas, there being no standard apparatus at hand. In such event, the tubes illustrated in Figure 5 can be quickly made up from plain glass tubing, of about 20 millimeters* (¾ inch) internal diameter. First bend and draw out the projecting end *d* of the tube A, retaining the conical form and making the external diameter about 4.7 millimeters ($^3/_{16}$ inch). Make the end corrugated so as to permit a rubber tube to be securely fastened thereon by wire, and have it project from the main tube some 38 millimeters (1½ inches) thus providing for the wooden stand *e*, which is to be slotted to allow of its receiving the tube, and of the latter being secured thereto by a clasp. This finished, cut the glass tube off to a length of about 500 millimeters (20 inches), and shape the end *c* down to an internal diameter

* To reduce millimeters to inches, multiply by .03937, or divide by 25.4.

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of about 0.8 millimeters ($^1/_{32}$ inch). Make this end 32 millimeters (1.25 inches) in length, and form its outside to correspond to the end *d* for a rubber tube connection. Next make up the tube A′ of similar diameter but one-third longer. The projection *d′* is identical with *d*, but

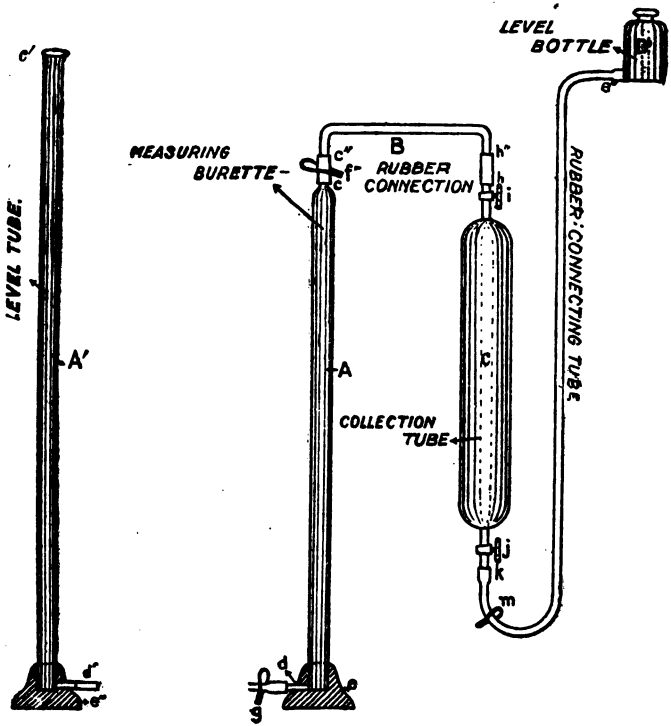

FIGURE 5.

at *c′* the tube, instead of being conically drawn out, as at *c*, is enlarged to a funnel shape, forming a mouth for the reception of liquids.

Having this complete, fasten a piece of seamless rubber tubing on the end *c* of the tube A by wire ligatures, leav-

ing some 40 millimeters (1.5 inches) of the tube length above the glass for the purpose of inserting a connecting piece thereon. Fasten the end of a piece of rubber tubing one-half meter (19.6 inches) long to the projection *d*, and a similar piece to the end *d'*, connecting the two free ends by a piece of glass tubing, thereby obviating the necessity of removing the wired ends at *d* and *d'* when cleaning the tubes. The tube A, which is termed the measuring burette, is thus connected to tube A', termed the level-tube.

To calibrate A, proceed as follows: First ascertain the amount of water contained by, say, 325 millimeters of the length of the tube A'. In this instance, as the internal diameter of the tubing is 20 millimeters, the quantity would be 102.102 cubic centimeters,* or each millimeter of the length of the tube would contain about 0.31416 cubic centimeters. Now fasten a thin strip of paper, scaled to millimeters, and about 400 millimeters in length, on the outside surface of the tube A', to serve temporarily. Place a pinch-cock, *f*, on the rubber tube close to the end *c*, and place another pinch-cock, *g*, in a similar manner on the rubber tubing close to the end *d*. With both pinch-cocks open, fill the two tubes with water, having the water overflow at the end of the rubber tube *c*, the capillary tubing B not being attached as yet; then close the pinch-cocks *f* and *g* and partially empty the level-tube A' so that the level of the water is a little above the lowest reading of the paper scale. Open the pinch-cock *g*, then by raising the level-tube A' so that the water in it will be on the same level as the water in the burette A (which is at the very top or end *c*), the contents of both tubes will be under equal pressure; *i. e.*, under equal atmospheric pressure. Notice at this time the reading of the water level in the level-tube A' on the improvised

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* To reduce cubic centimeters to cubic inches, divide by 16.383.

scale, taking care to read the position of the lowest point of the sharply defined, crescent-shaped meniscus formed at the surface of the water.

For the purpose of illustration, consider this reading to be 10 millimeters from the bottom of the scale. Now lower the level tube A', and open the pinch-cock *f* to admit air so as to allow the water in burette A to drop about 42 millimeters (1.6 inches) from its former level — the top of the tube at *c*. After waiting three minutes for the walls of the tube to drain, take the reading of the water level on the scale on level-tube A', under atmospheric pressure, by bringing the level of the water in both tubes to the same height. Suppose the reading to be 20 millimeters, then 20—10 (the former reading) = 10 millimeters, and as each millimeter was found to contain 0.31416 cubic centimeters, 10 millimeters would equal 10×0.31416 or 3.1416 cubic centimeters, the amount of air admitted.

Keep the level of the liquid in both tubes at the same height and then mark the line of water level on the burette A with a file. Now, in a similar manner as before, admit sufficient air to make a total of 100 cubic centimeters, which in the present case, would correspond to 318.3 millimeters in the scale of the level tube. In doing this no difficulty need be experienced if care is taken to admit very little air as the required amount (100 cubic centimeters) is approached. The level-tube A' should be raised frequently to make the readings until about the amount is obtained when three minutes should be allowed to drain the water from the walls of the burette before making the final measurement.

Now with the liquid in the level-tube A' and in the burette A at the same height, mark with a file the level of the water in burette A. This corresponds to 100 cubic centimeters, measuring from the top at *c*. Cut a strip of

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paper of a length equal to the distance between the two file marks, and on this paper lay off a scale in proportion, divisioning it into tenths of cubic centimeters, gluing it on to the measuring burette A and shellacking. The scale on the level-tube A′, may now be discarded, and there has been thus improvised an apparatus that, in lieu of a better one, will suffice for rough work.

Operation. The pinch-cocks *f* and *g* are first opened by simply slipping them off over the ends of the glass tubes *c* and *d*, and they remain so. Water is poured into the mouth *c′* of the level-tube A′, until it overflows from the short rubber tube on *c*, when the pinch-cocks *f* and *g* should both be closed. During the operation of filling with water, the level-tube A′ should be held at such a height with respect to the burette A, that it may fill the former about two-thirds full. Now make connection with the collection tube C, containing the gas sample, by means of the capillary tube B, which should be as short as possible and bent at right angles at a point about 30 millimeters from each end. In joining the capillary tube B, first prepare it by filling with water and wiping a little vaseline over the ends *c″* and *h″* where the rubber tube connections are to be attached. By means of a small dropping pipette also fill with water the short pieces of rubber tubing in the ends *c* and *h* of the burette and collection tube respectively, and by slipping one end of the capillary tube into the rubber tube at *c* and the other end into the end of the rubber tube at *h*, all air will be excluded. The end *k* of the collection tube C should be connected by a piece of rubber tubing a meter (39.37 inches) long to the level-bottle D, after which slip a pinch-cock *m* on the rubber tube near *k*.

The above connections having been made, next place the level-tube A′ on the floor with burette A resting on a stand, and raise the level-bottle D to a support arranged

above the collection tube C. Open the pinch-cocks *g*, *f* and *m* and the glass-cock *j* in the collection tube C, thereby putting the collection tube C and level-bottle D in connection. By opening the glass cock *i* the pressure of the column of water between the collection tube and the level-bottle will force the gas over into the burette A, and in this it will be assisted by the expansion of the water in A, due to the relatively low position of level-tube A'. Pass over about 50 cubic centimeters of gas, close the glass-cock *i*, and agitate the water in the burette vigorously in order that it may become saturated with the gas. Next open the glass-cock *i*, raise the level-tube A' and lower level-bottle D, causing the gas to return to the collection tube. Agitate the collection tube, after which transfer the gas back and forth a few times, thoroughly saturating the water in both the level-bottle and level-tube, to prevent the water washing out the soluble constituents of the gas when making the analysis.*

This preliminary operation complete, force all the gas from the burette A by raising the level-tube A' and lowering the level-bottle D. Close the pinch-cocks *f* and *m* and the glass-cocks *i* and *j*, and disconnect the rubber tubing of the level-bottle D from the collection tube—the pinch-cock *m* serving to prevent the out-flow of water; also remove capillary B from both the collection tube and burette. Fill the short rubber tube at *c* and the capillary tube B with water, and after wiping the ends of the latter with vaseline, make connections with a new collection tube, containing sample gas.

One is now ready to proceed with the analysis proper.

Analysis. By lowering the level-tube and raising the level-bottle, opening pinch-cocks *f* and *m* and glass-cocks *i* and *j*, about 103 cubic centimeters of gas is admitted to

* With the present apparatus this is almost a useless precaution, but is given to familiarize the reader with principles to be followed in more exact analyses.

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the burette, when pinch-cock *f* and glass-cocks *i* and *j* are closed, the capillary tube disconnected, and, together with the collection tube and level-bottle, laid aside. Close pinch-cock *g* and place level-tube on the support above, thereby creating a pressure due to the weight of the water column above the water level in the burette. After waiting three minutes for the walls of the burette to drain, open pinch-cock *g* just sufficient to allow the lowest point of the meniscus of the water to rise to the 100 cubic centimeter mark in the burette, taking precaution to have the eyes on the same level. There is now contained in the burette 100 cubic centimeters of gas under pressure a trifle greater than atmospheric. Open pinch-cock *f* to the air for but a moment, thus allowing the excess pressure to escape. By now opening pinch-cock *g* and holding the level-tube so that the surface of the liquid therein will be on the same level with the liquid in the burette, thus putting our gas under atmospheric pressure, the level in the burette will be found to coincide with the 100 cubic centimeter mark.

In these illustrations, 100 cubic centimeters of gas is taken to simplify matters, as the readings thus give percentages direct.

Determination of Carbon Dioxide. We first determine the quantity of carbon dioxide (chemical formula CO_2) by absorption with a reagent.* The reagent used as an absorbent may be potassium hydroxide, sodium hydroxide, or barium hydroxide. The first is to be preferred, owing to its quick action, but the last is employed to advantage when the quantity of carbon dioxide is very small.

To treat the gas with the reagent, lower the level-tube to expand the gas in the burette until the level of the water

* Most of the constituents of coal gas may be removed or absorbed by certain liquid reagents, there being exceptions, however, such as hydrogen, methane, nitrogen, etc., which are removed by combustion.

lowers almost to the top of foot-piece *e*; then close pinch-cock *g*, and empty the level-tube and tubing of water and then partially replace it with the absorbent. Raise the level-tube with the left hand as high as the rubber tubing permits, when, by opening pinch-cock *g*, a considerable quantity, diluted with the water left in the rubber tubing, will be forced into the burette. Lowering and raising the level-tube will thoroughly mix the reagent and the water and assist in the absorption of the carbon dioxide. By closing pinch-cock *g* and agitating the burette, all the gas will be brought into intimate contact with the absorbent. Note the readings from time to time, and when no further diminution of volume takes place, open pinch-cock *g*, and after waiting three minutes for the walls of the burette to drain, measure the gas volume under atmospheric pressure by bringing the level of the liquid in both tubes to the same height. This reading, subtracted from 100, will give the per cent. by volume of carbon dioxide in the gas.

Determination of Illuminants. Again lower the gas in the burette as much as possible, and in doing so, exercise the same care as before in order to prevent the liquid in the burette from dropping too low lest the gas gets into the tube and escapes. Then close the pinch-cock *g*, and empty the level-tube of the reagent, afterwards rinsing out with water. Next, add a little water in which a few drops of hydrochloric acid was previously mixed, to neutralize the remaining reagent in the lower portion of the burette.

The next determination is that of the illuminants or heavy hydrocarbons. These consist principally of ethylene, (formula C_2H_4) the absorbent for which is bromine water. The level tube is nearly filled with water and a little bromine is added with a dropping pipette. The gas residue is then treated with this reagent as in the previous case until no further action takes place. In the

present instance, however, before measuring the amount of absorption, it will be necessary to empty the level-tube of the bromine water, first closing pinch-cock *g*, and then partially replacing, not with the next reagent, but with potassium hydroxide, with which treat the gas. This is necessary after using bromine, owing to its high tension, or tendency to vaporize. The potassium hydroxide absorbs this vapor, after which the gas may be measured and the true percentage of ethylene may be ascertained by direct reading.

Determination of Oxygen. Again lowering the gas in the burette and emptying the level-tube, rinse and partially fill with potassium pyrogallate for the absorption of oxygen, (symbol O). The method of treatment in this case is similar to the preceding, except that no vapors are formed, and, in consequence, treatment with potassium pyrogallate alone suffices.

Determination of Carbon Monoxide. The percentage of oxygen determined, empty the level-tube, rinse with water, and add the next absorbent, cuprous chloride, for the absorption of carbon monoxide, (formula CO). This is our last determination with this apparatus. An example may serve to illustrate the foregoing operations.

Partial analysis of Dowson producer gas:

The water in level-tube and level-bottle was saturated with the gas.

From another collection tube 100 cubic centimeters of the sample gas was taken for analysis.

After treating with potassium hydroxide until no further absorption took place, the gas volume measured 93.43 cubic centimeters; hence, $100-93.43=6.57$ cubic centimeters, the amount of carbon dioxide in 100 cubic centimeters of sample gas, or, carbon dioxide is 6.57 per cent.

Level-tube emptied, rinsed with water, and a little hydrochloric acid added to neutralize the potassium hy-

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droxide. Gas is treated with bromine water until absorption is complete, level-tube then emptied, rinsed, and partially filled with potassium hydroxide to absorb the bromine vapors. Gas volume then measured 93.12 cubic centimeters; hence, 93.43 (last reading) $-93.12=0.31$ cubic centimeters, the amount of ethylene present in 100 cubic centimeters of sample gas, or, ethylene is 0.31 per cent.

Level-tube emptied and rinsed, and without adding hydrochloric acid, gas is treated with potassium pyrogallate until no further absorption, and volume then measured 93.09 cubic centimeters; hence, 93.12 (last reading) $-93.09=0.03$ cubic centimeters, the amount of oxygen present in 100 cubic centimeters of sample gas, or, oxygen is 0.03 per cent.

Level-tube emptied, rinsed, and gas treated with cuprous chloride until no further absorption. Gas volume was 68.02 cubic centimeters; hence, 93.09 (last reading) $-68.02=25.07$ cubic centimeters, the amount of carbon monoxide present in 100 cubic centimeters of sample gas, or, carbon monoxide is 25.07 per cent.

Other constituents of the gas could not be determined with this apparatus. They must be determined by combustion, as will be shown later. This apparatus would suffice, however, for furnace or chimney gases composed of carbon dioxide, oxygen, carbon monoxide, and nitrogen. The nitrogen in this case would be found by difference; *i. e.*, by subtracting the sum of the other gases from 100, which would give its percentage.

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Chapter III.—THE ORSAT APPARATUS.

Examination of Furnace or Chimney Gases by means of the Orsat Apparatus. With the apparatus already considered, the gas was drawn into a measuring burette and successively treated by the absorbents, which (in the case of potassium pyrogallate and cuprous chloride), owing to exposure to the oxygen of the air during the treatment, could be used but a few times before their powers of absorption became exhausted.

Orsat devised an apparatus whereby the reagents are protected from the air, and in which the gas itself is brought in contact with the absorbents. It is only to be regretted that the scope of the apparatus is so limited. It offers, however, a most convenient means for the determination of carbon dioxide, oxygen, and carbon monoxide by absorption, and nitrogen by difference, these being the gases found as constituents in furnace and chimney analyses.

Description. Consists of three double pipettes, B, C, and D, Figure 2, made stationary in the case and connected by means of capillary tubing to a measuring burette A, enclosed by a water jacket. Glass stop-cocks E, F, and G close each pipette to the main capillary, and the glass stop-cock H, thereon, affords an inlet for air from the end J. A level-bottle L, provides a means of transferring the gas. To the rear of the pipettes B, C, and D, and connected by glass tubing, are three similar pipettes, whose ends, s, s', and s'', are connected by rubber tubing with a small, flexible rubber bag, which acts as a seal, preventing the absorption of oxygen from the air by the reagents in the pipettes. The water-jacket may,

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under ordinary conditions, be simply filled with water, which will tend to prevent slight changes of temperature affecting the gas volume. When the apparatus is so situated as to be subject to draughts or sudden changes,

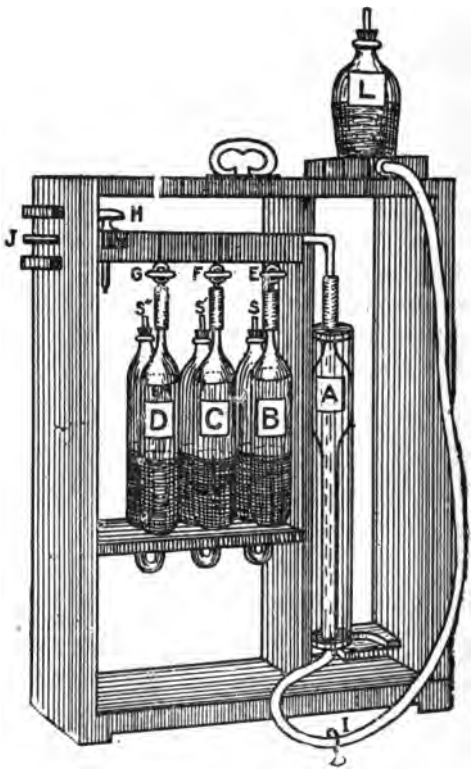

FIGURE 6.

—although this should be avoided when possible—connections should be made with the water supply, so as to have a circulation of water in the jacket, which will secure a fairly even temperature.

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Figure 6 shows Fisher's modification of the Orsat,

which is of small size and arranged for convenience in traveling.

Figure 7 shows a slight modification known as Petrizilka's, with one universal stop-cock, dispensing with the four small ones.

Manipulation. The level-bottle L is filled with pure water, and with stop-cocks E, F, and G closed, and H

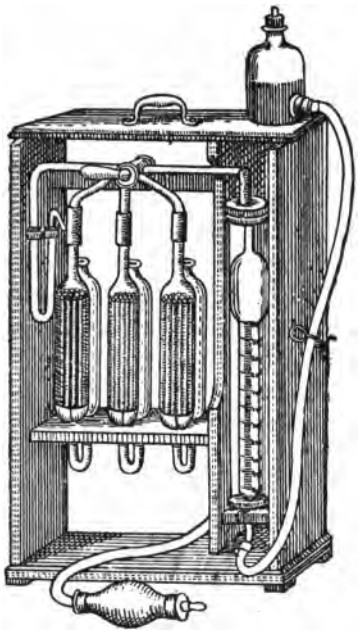

FIGURE 7.

opened, and the measuring burette is partly filled by raising level-bottle L, forcing air through exit J. By closing stop-cock H and lowering level-bottle L, the air remaining in the burette and capillary is expanded, so that on opening stop-cock E, the reagent in pipette B will be drawn up to

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a point just below the connecting rubber M, when stop-cock E is closed and the reagents in pipettes C and D similarly raised to corresponding positions. This done, open stop-cock H, and by raising level-bottle L, force all the air from both the burette A and the capillary tubing, displacing by water which will overflow from the end of capillary at J, when close stop-cock H.

Preliminary to the analysis proper, make connections with a collection tube of sample gas and the end J, of capillary tubing of the apparatus, taking same precautions as before, with previous apparatus, to expel all air from the rubber tube and connecting tube, if one is used. Draw in about 50 cubic centimeters of gas (there is contained 100 cubic centimeters from the stop-cock H in the capillary tube, to a point marked 100 cubic centimeters near the bottom of the burette, and the graduations are in tenths of cubic centimeters), by lowering level-bottle L. As soon as the gas is admitted, close stop-cock H, and raise and lower the level-bottle to cause the gas to come in through contact with the water, thus saturating the latter with the absorbable constituents of the gas. Open stop-cock H and expel the gas, filling completely the burette and capillary with the saturated water, and on its overflowing at J close the stop-cock H. We are now ready for our sample for analysis, so make connections with a new collection tube and draw in through end J, in a similar manner, a little more than 100 cubic centimeters,—say, for instance, 101 cubic centimeters—closing stop-cock H immediately on securing that amount. Wait one minute for the walls of the burette to drain, and then close the pinch-cock I on the rubber tube connecting the level-bottle and the burette, close to the latter. By raising the level-bottle L, a pressure is created, due to the height of the column of water, so that on gradually opening the pinch-cock I, the gas is forced up in the burette. With the eyes on the

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level of the 100 cubic centimeter mark on the burette, close the pinch-cock I just as the lowest point of the meniscus reaches the mark, when we will have 100 cubic centimeters of gas at little more than atmospheric pressure. By opening the stop-cock H for but a moment, this excess will escape to the air, leaving us exactly 100 cubic centimeters of gas. By opening pinch-cock J and bringing the level-bottle L to such position that the level of the liquid contained corresponds to the level of the liquid in the burette, we will find that the level in the burette will be at the 100 cubic centimeter mark, proving the amount of gas contained to be 100 cubic centimeters at atmospheric pressure.

Determination of Carbon Dioxide. We may now treat our gas to the first absorbent, potassium hydroxide, which is contained in pipette B. Opening stop-cock E and raising level-bottle L, forces the reagent down the front and up into the rear pipette, laying bare the contained tubes, wet with the reagent, thus exposing a large absorbing surface. This reagent quickly absorbs the carbon dioxide present in the gas, one passage of the gas into the pipette generally proving sufficient. By raising and lowering the level-bottle a few times all the gas is brought into thorough contact with the absorbent, and can then be drawn back into the burette for measurement by lowering the level-bottle L, closing stop-cock E, when the reagent has ascended to its former position close to the rubber connection. After waiting one minute for the walls of the burette to drain, bring the level of the liquid in level-bottle and burette to the same height, and read the position of the lowest point of the meniscus on the scale, giving the quantity of carbon dioxide absorbed. Again pass the gas into the pipette B, return to burette, (closing stop-cock E as before) and measure, after waiting one minute for burette to drain. See if this reading corresponds to

the former, to make certain that the absorption is complete. This reading, subtracted from 100, the total volume of sample gas, gives the percentage of carbon dioxide.

Determination of Oxygen. The residue, or gas remaining from the last absorption, is now passed into the second pipette C, containing potassium pyrogallate, which absorbs the oxygen. Before making the final measurement, the operation should be repeated as in the previous case, to make certain that all the oxygen is absorbed. The time required will not exceed three minutes. In making the reading first allow one minute for walls of burette to drain, this being done whenever a measurement is to be made. The reading in this case subtracted from the previous one, gives the percentage of oxygen.

Determination of Carbon Monoxide. The residue is now passed into the third pipette D, containing cuprous chloride, which absorbs the carbon monoxide. A little more time should be given to this absorption, which is somewhat uncertain; say, at least five minutes. The resulting reading, subtracted from the previous one (with potassium pyrogallate), gives the percentage of carbon monoxide.

Determination of Nitrogen. Adding the percentages of carbon dioxide, oxygen, and carbon monoxide together, and subtracting the total from 100, gives the percentage of nitrogen by difference.

Special Hints. In the foregoing operations always pass the gas into the pipettes in the order named, since potassium pyrogallate, contained by the second pipette, will absorb both oxygen and carbon dioxide; and cuprous chloride, of the third pipette, both carbon monoxide and oxygen.

Before measuring and after each absorption, wait some stated interval, making it of the same duration throughout, for the walls of the burette to drain of liquid, since otherwise the readings would be in error.

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The total time required will usually be about twenty minutes for the entire analysis.

An accurate account of the cubic centimeters of absorption with each reagent should be kept, and by comparing with the absorbing capacities, one will constantly know the power of the reagent, so that he may renew it as its strength becomes taxed.

The capillary tubing of the Orsat apparatus, shown in Figure 6, being two millimeters internal diameter, it requires 31.8 millimeters of length (1.25 inches), to give one-tenth of a cubic centimeter. Thus, error due to the reagents not being exactly on the mark, will be slight.

To prevent the glass stop-cocks from becoming fast in their sockets, which often causes fracture on attempts at freeing, keep well lubricated with a mixture of one part tallow and three parts vaseline.

No trouble need be experienced in the use of this apparatus, even by one unfamiliar with chemical work or analysis.

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Chapter IV.—THE ELLIOTT APPARATUS.

By means of the apparatus already described, it was only possible to analyze a mixture of gases containing carbon dioxide, ethylene (illuminants), oxygen, and carbon monoxide. When it is desirable to ascertain the composition of a mixture containing hydrogen or methane as found in producer gas, illuminating gas, etc., recourse must be had to apparatus which affords a means of burning these gases with oxygen, a measurement of the products of combustion, together with the contraction, enabling one to compute the volumes burned. With Dr. Elliott's apparatus such a determination may be made very rapidly, although at the expense of great accuracy. Owing to the explosion, over water, of the residual gas (the portion remaining after the absorbable constituents are removed), the error of results may be as great as two per cent., although the total error may generally be kept within one per cent., which will meet the requirements of technical work. In iron and steel works, metallurgical establishments, for glass-ovens, and regenerative furnaces using producer gas, and for the analysis of chimney or flue gases, the "Elliott" makes possible sufficiently rapid work to enable the operator to keep in constant touch with the various changes taking place.

The principal innovation with this apparatus lies in the treatment of the gases by permitting the reagents to spread and run down the sides of a long tube containing the gas mixture, bringing the absorbent in intimate contact with loss of but little time.

Description. It consists of an absorption tube A (Figure 4), measuring burette B, and explosion burette C, all graduated to 100 cubic centimeters, although of but one-half

the indicated capacity. The two burettes, B and C, are divisioned in tenths of cubic centimeters. The bulbs, at the junction of the tubes A and B with the capillary tubing, serve to render the apparatus more compact by lessening the height, and, in the case of the absorption tube A, provides a means of spreading the liquid reagents used. At the lower end of the absorption tube A is inserted, by means of a cork C',* an arm of capillary tubing, which communicates by the three-way stop-cock D' with the level-bottle M, through the arm E' and rubber tubing fastened thereon, and affords an exit for the discharge of reagents by way of the arm V. Above the horizontal capillary on the tube A is a stop-cock B' communicating with the open end A', ground tapering to receive the funnel F' by which the reagents are introduced. The horizontal capillary just below is cut off square at the ends I' and J' to permit of a piece of glass capillary tubing G, being inserted to form a close joint with a short piece of rubber tubing H holding it in place. A similar arrangement is provided for the ends K' and L', thus connecting the three tubes. The lower ends of the measuring and explosion burettes are drawn out to receive rubber tubing with which to connect with the level-bottles N and P. It is advisable to fasten the rubber tubing on the projecting ends by wire ligatures, necessitating the use of three level-bottles, which is preferable, in the writer's opinion, to loose connections and frequent interchange, as is the case when but two are used, as supplied by the makers.

Near the lower end of the explosion burette, below the rubber stopper R' of the water-jacket W, projects an arm of capillary tubing U' with a stop-cock T', through which to introduce the air and oxygen (or hydrogen) used in the combustion of the residual gas. Above the rubber

*A recent modification, making the absorption tube and capillary of one piece, does away with this cork.

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stopper Q of the water-jacket, are fused two platinum wires P' for an ignition spark. The water-jacket W serves to prevent undue heating of the burette during combustion, saving time which would otherwise be required for its cooling. As directed in connection with the Orsat, when

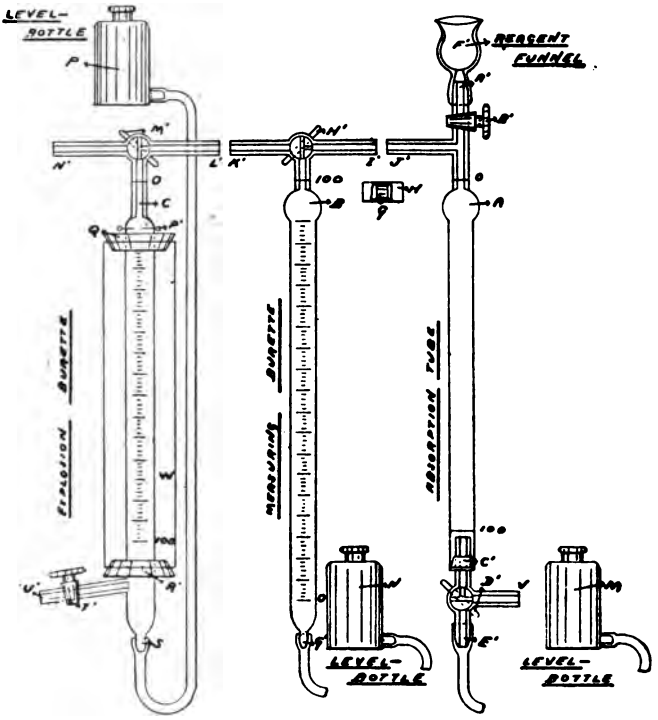

FIGURE 8.

the measuring burette is subject to changes of temperature during an analysis, it should also be water-jacketed. The explosion burette is made of heavy glass and there is consequently but little liability to fracture with the exercise of proper care during the explosion.

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Operation. Before commencing an analysis, about two

liters (approximately two quarts) of water should be saturated with the gas under examination, to prevent, as far as possible, the washing out of the soluble constituents of the gas mixture, previous to their absorption by the reagents. With this apparatus the gas is successively treated with the absorbents, as was done with the improvised tubes shown in Figure 5, differing in this respect from the Orsat. The absorptions are made in the absorption tube A (Figure 8), and the subsequent measurements in the burette B. In preparing for the analysis the level-bottles M, N and P are nearly filled with the saturated water, the connections on the horizontal capillary tubing between the ends J′ and I′, K′ and L′ being made, stop-cocks D′, H′ and M′ are opened to give a passage between the level-bottle M and absorption tube, and both through the horizontal capillary and into the measuring and explosion burettes. A rubber tube should be fastened on the end V of the projecting arm from the stop-cock D′, to carry off the waste liquids to the drain.

Open stop-cock B′ and raise all three level-bottles, filling the entire apparatus with water, thereby expelling all air. Close three-way cock M′ so that the run is just closed to the capillary, bringing the outlet up, the reverse of the former position. (In speaking of three-way stop-cocks the long or through passage will be termed the "run," and the branch at right angles to this the "outlet.") Close stop-cock H′ so that the run and outlet are closed to the capillary and measuring burette respectively, with the outlet down. Close stop-cock B′, taking care that the water overflows at the end A′. Open stop-cock T′ on the explosion burette to allow the air, caught in the capillary portion, to escape; close when water overflows at the end U′. We are now ready to admit the gas sample.

Connection is made at end A′ of the absorption tube with the gas source. The level-bottle M is lowered and

stop-cock B′ opened to admit a little more than 100 cubic centimeters of gas. (The actual amount admitted will be a little more than 50 cubic centimeters, inasmuch as all three tubes are graduated to read double the capacity to avoid computation in deriving the percentages.) With stop-cock B′ closed, open stop-cock H′ bringing the outlet up to the main capillary, and the run up and down (the position shown in Figure 4), when connection will be made between the absorption tube and measuring burette. Raise level-bottle M and lower level-bottle N, causing the gas to pass into the burette. Now raise the level-bottle N to a height that will bring the level of the water therein to the zero or lowest graduation on the scale of the burette B. Retain in this position, and after waiting one minute for the walls of the burette to drain, lower level-bottle M a little, causing the water in the burette B to rise to the zero mark; then close stop-cock H′ with the outlet up, when the burette will contain exactly 100 cubic centimeters of gas under atmospheric pressure. The error due to the capillary tubing between the 100 cubic centimeter mark and the stop-cock H′ is of no consequence, since the tubing in this half-sized apparatus is but one millimeter internal diameter, requiring 127.3 millimeters (5 inches) of length to give one-tenth of one cubic centimeter. It might be remarked here that any error consequent upon the retention of air in the capillary tubing, will be slight, but may be readily estimated by measuring the length of the air bubble. The gas remaining in the capillary and absorption tube may now be expelled by raising level-bottle M, opening stop-cocks H′ and M′, to make connections with exit N′ (having the outlets of the three-way cocks up) and stop-cock B′, closing all three, on the overflow of water, to their former positions. Transfer the 100 cubic centimeters of gas by raising the level-bottle N, lowering the level-bottle M, and opening stop-cock H′, so that it communicates with the

absorption tube. Have the water rise in the measuring burette until it reaches the absorption tube end of the horizontal capillary, thus causing all the gas to pass over, when stop-cock H′ is to be closed, with outlet up. Place the funnel F′ on the end A′, noticing whether there is any air in the vertical capillary; if so, it can be dislodged by inserting a copper wire, with a little water in the funnel. We are now ready to treat the gas with the reagents.

Determination of Carbon Dioxide. The first determination is, as in former instances, that of the carbon dioxide. The reagent, potassium hydroxide, is poured into the funnel F′, filling the latter about two-thirds full, before opening the stop-cock B′ just enough to allow of the reagent spreading evenly around the bulbed portion of the absorption tube A, and running slowly down the sides. Never allow the reagent in the funnel to quite reach the top of the vertical tube, lest air be admitted. Sufficient of the potassium hydroxide should be added to suit the requirements of the gas under examination, a very little sufficing as a rule. On the admission of the proper amount, close stop-cock B′ and transfer the gas to the measuring burette by opening stop-cock H′ and raising and lowering level-bottles M and N respectively, closing stop-cock H′ as soon as the water from the absorption tube reaches the vertical capillary of the measuring burette. Wait one minute before making the measurement, for the walls of the burette to drain; then, with the level of the water in the measuring burette and level-bottle N at the same height, note the position of the lowest point of the meniscus at the surface of the water, with refererence to the graduations of the scale. This gives the reading under atmospheric pressure, and subtracted from 100, gives the amount of absorption. Transfer the gas to the absorption tube by opening stop-cock H′, raising level-bottle N and lowering level-bottle M, and again treat with potas-

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sium hydroxide. Transfer to measuring burette and take the reading under atmospheric pressure. If this corresponds to the former reading, the absorption is complete; if not, more reagent must be added until two consecutive readings agree. It is seldom that one treatment does not suffice, but this precaution should be taken after each absorption. With the gas in the measuring burette, turn the stop-cock D′ so that it communicates with the drain V (position shown in Figure 4); open stop-cock B′ and add water through the funnel F′, rinsing all reagent from the tube. With the tube clean, turn stop-cock D′ to shut off the drain and connect the level-bottle and absorption tube; open stop-cocks H′ and M′ to the horizontal capillary, with outlets up, and raising level-bottle M, fill the absorption tube and capillary with water, closing stop-cocks M′, H′ and B′ as the water overflows from the exit N′ and the end A′ of the vertical tube. Transfer the gas to the absorption tube.

Determination of Illuminants. Fill the funnel F′ two-thirds full with water, and with a small dropping pipette add a few drops of bromine. Partly open stop-cock B′, allowing the bromine water to spread around the bulb and flow down the sides of the absorption tube. The tension of bromine being high, the tube will quickly fill with vapor, when the stop-cock B′ should be closed. Before transferring to the burette for measurement, add potassium hydroxide (emptying funnel of any bromine water remaining) to absorb the bromine vapors, and then transfer the gas to the measuring burette. Note the reading, which, subtracted from the previous one, gives the percentage of illuminants.

Determination of Oxygen. With the gas in the measuring burette, rinse the absorption tube and capillary well out with water and refill. Transfer the gas to the absorption tube and treat with the next reagent, potassium py-

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rogallate. Measure the amount of absorption in the measuring burette. This reading, subtracted from the last one, gives the percentage of oxygen.

Determination of Carbon Monoxide. Having rinsed the absorption tube and capillary of the last reagent and filled with water, transfer the gas from the measuring burette and treat with cuprous chloride. After using this, and previous to transferring the gas for measurement, add water to absorb the acid vapors. Transfer, and note the reading, which, subtracted from the last, gives the percentage of carbon monoxide. Especial care should be exercised to make this absorption complete.

The gas residue, sometimes termed gas rest, or portion remaining after the absorbable constituents have been removed, may consist of hydrogen, methane, and nitrogen. The explosion or combustion tube is employed for their determination, since in their combination with oxygen there is a resulting contraction, which, together with the volume of carbon dioxide formed, affords sufficient data for the computation of the volume burned.

Operation. The gas residue is retained in the measuring burette; with the stop-cock H′ (Figure 8) closed to the burette B and open to the horizontal capillary, adjust stop-cock M′ so that it communicates with the explosion burette, absorption tube and outlet N′. By raising the level-bottles M and P, force any air from the capillary, completely filling the entire apparatus with the exception of the measuring burette containing the gas residue, with water, when close stop-cock M′ to both burette and capillary, the outlet toward the right. Raise level-bottle N, turn stop-cock H′ so as to bring the outlet open to the capillary in the direction of the explosion burette, lower level-bottle P, open stop-cock M′ so that it makes connection between the explosion and measuring burettes (position shown in cut), and admit to the former some 15 cubic centimeters of the

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residual gas, by the graduations on the explosion burette. Close stop-cock H′ by bringing to the position with the outlet in the direction of the explosion burette just closed, and after waiting one minute for the walls to drain, raise level-bottle P so that the level of the contained water will correspond to that in the explosion burette, and note the reading, giving the volume of the sample of residual gas under atmospheric pressure. Since the determination of the constituents of the residual gas is by means of combustion or chemical union with oxygen, sufficient of the latter must be admitted to supply the hydrogen and methane, the nitrogen remaining inert. Hydrogen requires one-half its volume of oxygen for complete combustion, and methane requires twice its volume, consequently, with an approximate knowledge of the amounts of these constituents present, it is a simple matter to decide upon the quantity of oxygen required taking care to admit in excess.

With but a knowledge of the kind of gas under examination, whether coal, water, or producer gas, etc., one will be sufficiently guided after a little experience. The oxygen is admitted partly as free air, (air is about 22 per cent. oxygen by volume), and partly as pure oxygen. Generally speaking, for illuminating gas the air used should equal the volume of the gas sample. This may be admitted through the stop-cock T′ at the lower end of the explosion burette, but more conveniently through the capillary N′ and stop-cock M′ by expanding the gas in the explosion burette by lowering level-bottle P. After admitting the air, make connection between the end U′ of the projecting capillary and the supply of oxygen.* Open stop-cock T′, admitting sufficient oxygen to make a total gas volume of

*The oxygen may be prepared by heating a mixture of four parts, by weight, of potassium chlorate and one part of manganese dioxide, in a generator supplied for this purpose, and collecting in a gas holder in which the gas should be put under a slight pressure.

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about 75 cubic centimeters, when close stop-cock T' and raise and lower level-bottle P, causing the gas to become thoroughly mixed, also dislodging any oxygen caught in the capillary above the stop-cock T'. Wait one minute for the burette walls to drain, then measure the total gas volume under atmospheric pressure. Dislodge any water adhering to the ends of the platinum wires by tapping the tube slightly. Lower the level-bottle P as far as possible to expand the gas, thus tending to render the explosion less severe. With all precautions there is a possibility of fracture at this time; it is therefore best not to expose the eyes. Make connection to the induction coil and battery, closing the circuit, causing a spark to pass between the points of the wires, thereby igniting the gas, which gives a sharp click.

Allow the heat of the combustion to be absorbed by the circulating water in the jacket and then take the reading of the gas volume under atmospheric pressure. This, subtracted from the reading of total gas volume taken before the explosion, gives the contraction, which, for future reference, we will call C. Now raise level-bottle P, lower level-bottle M, and noting that the horizontal capillary and absorption tube are filled with water, transfer the products of combustion from the explosion burette to the absorption tube, where treatment with potassium hydroxide will absorb the carbon dioxide formed. After treatment with the absorbent, transfer back to the explosion burette, and, after waiting one minute for the walls of the burette to drain, measure, under atmospheric pressure, the amount of absorption. Let the amount, which equals the carbon dioxide formed, be called D. We now have sufficient data to determine the percentage of hydrogen and methane directly, and the nitrogen by difference.

The chemical reaction of hydrogen with oxygen is expressed by the following equation:

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$$\underset{\text{Hydrogen}}{H_2} + \underset{\text{Oxygen}}{(O_2)_{\frac{1}{2}}} = \underset{\text{Water}}{H_2O} \quad \text{(Equation 1)}$$

One volume of hydrogen unites with one-half volume of oxygen, forming water, which, in changing from a gaseous to a liquid form, contracts so as to be of no appreciable volume, hence its volume may be neglected; we have then, 1 volume + ½ volume, or 1½ volumes contracting to zero volumes; or, the amount of contraction equals 1½ volumes, which is 1½ times the amount of hydrogen burned. (1½H).

The reaction of methane with oxygen is expressed by the equation:

$$\underset{\text{Methane}}{CH_4} + \underset{\text{Oxygen}}{(O_2)_2} = \underset{\text{Carbon Dioxide}}{CO_2} + \underset{\text{Water}}{2H_2O} \quad \text{(Equation 2)}$$

One volume of methane uniting with two volumes of oxygen, forming one volume of carbon dioxide and water. As before, the water volume is neglected, hence we have 1 volume + 2 volumes, or 3 volumes; contracting to 1 volume, or the amount of contraction equals 2 volumes, which is 2 times the volume of methane burned. ($2CH_4$). There is one volume of carbon dioxide formed for each volume of methane burned, or $CO_2 = CH_4$.

Collecting from equations 1 and 2, we have

$$C = 1\tfrac{1}{2}H + 2CH_4 \quad \text{(Equation 3)}$$

$$D = 1CH_4 \quad \text{(Equation 4)}$$

in which C = the total contraction resulting from the combustion of the residual gas, and D = the carbon dioxide formed.

C, the contraction, is known as measured in the explosion burette, also D, the carbon dioxide formed, the amount of which was determined by absorption with potassium hydroxide; substituting for CH_4 in equation 3, its value D, from equation 4, we have

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$$C = 1\tfrac{1}{2}H + 2D, \text{ or, } H = \frac{C - 2D}{\frac{3}{2}} = \frac{2C - 4D}{3} \quad \text{(Eq. 5)}$$

By substituting for D in equation 4, and for D and C in equation 5, their values, the per cents of methane and hydrogen become known.

The sum total of the per cents so far determined, subtracted from 100, gives the percentage of nitrogen. An example will serve to illustrate the entire proceeding:

Analysis of Coal Gas. A two-liter bottle of water was first saturated with the gas to be examined. The level-bottles and apparatus were then filled with the prepared water, expelling all air. A little more than 100 cubic centimeters of sample gas was drawn into the absorption tube, and afterward transferred to the measuring burette, where exactly 100 cubic centimeters, measured under atmospheric pressure, was retained, the excess being expelled by filling the apparatus with water from the level-bottles.

Gas then transferred to the absorption tube, where it was treated with potassium hydroxide, the first reagent.

Gas returned to the burette, and, after waiting one minute for drainage of walls, measured under atmospheric pressure, giving a reading of 99.5. This, subtracted from 100, gave the percentage of carbon dioxide:

$$100 - 99.5 = 0.5, \text{ or, } CO_2 = \tfrac{1}{2} \text{ of } 1 \text{ per cent.}$$

The absorption tube was drained of the reagent, rinsed, and refilled with water. Gas then transferred to the absorption tube and treated with bromine water, the second reagent. As soon as the absorption was complete, potassium hydroxide was added to absorb the bromine vapors formed. Gas then returned to the burette and measured under atmospheric pressure, giving a reading of 95.5. This, subtracted from the previous one, 99.5, gave the per cent. of illuminants:

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99.5 — 95.5 = 4, or, illuminants, 4 per cent.

The absorption tube was then drained of the reagent, rinsed and refilled with water.

Gas then transferred to the absorption tube and treated with potassium pyrogallate, the third reagent.

Gas returned to burette and measured under atmospheric pressure, giving a reading of 95. This, subtracted from the previous one, 95.5, gave the percentage of oxygen:

95.5 — 95 = 0.5, or, O = ½ of 1 per cent.

The absorption tube was drained of the last reagent, rinsed, and refilled with water.

Gas then transferred to the absorption tube and treated with cuprous chloride, the fourth reagent. Afterwards water was added to absorb the acid vapors and wash down the curdy, white precipitate of cuprous chloride.

Gas returned to burette and measured under atmospheric pressure, giving a reading of 89. This, subtracted from the previous one, 95, gave the percentage of carbon monoxide:

95 — 89 = 6, or, CO = 6 per cent.

The absorption tube was drained of the last reagent, rinsed, and refilled with water.

A portion of the gas now remaining, termed the residual gas, was transferred to the explosion burette, and on measuring was found to be 18 cubic centimeters. To this was added about 15 cubic centimeters of air and then oxygen sufficient to bring the total volume to 80 cubic centimeters, all measured under atmospheric pressure. By raising and lowering the level-bottle these gases were thoroughly mixed. A slight tapping dislodged the water adhering to the points of the platinum wires. The gas mixture was expanded by lowering the level-bottle as far as the rubber tubing would permit, thereby lessening the intensity of the explosion. On closing the circuit a sharp

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click was heard, giving assurance that the explosion occurred.

After a lapse of three minutes, the gas was measured under atmospheric pressure, giving a reading of 49.53. This, subtracted from 80, the amount burned, gave the contraction: $80 - 49.53 = 30.47$.

The products of the combustion, or gas remaining in the explosion burette, was transferred to the absorption tube and treated with potassium hydroxide.

Gas returned to the explosion burette and measured under atmospheric pressure, giving a reading of 41.43. This, subtracted from the previous one, 49.53, gave the amount of carbon dioxide formed by the combustion of the gas residue:

$49.53 - 41.43 = 8.1$, or, the $CO_2 = 8.1$ cubic centimeters, and CH_4 present in 18 cubic centimeters of residual gas equals 8.1 cubic centimeters, since $CH_4 = D = CO_2$, by equation 4.

For the total amount of residual gas, 89 cubic centimeters, the methane would equal, by simple proportion:

$18 : 89 :: 8.1 : X$; $X = 40.05$, or, $CH_4 = 40.05$ per cent.

The hydrogen is computed from equation 5:

$$H = \frac{2C - 4D}{3} = \frac{2(30.47) - 4(8.1)}{3} = 9.51$$

or the hydrogen present in 18 cubic centimeters of residual gas equals 9.51 cubic centimeters; hence for the total volume of residual gas, 89 cubic centimeters, we have by simple proportion

$18 : 89 :: 9.51 : Y$; $Y = 47.02$, or $H = 47.02$ per cent.

All the constituents of the sample gas have now been determined, with the exception of nitrogen, which may be found by difference as follows:

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CO_2	= 0.50
C_2H_4 (illuminants)	= 4.00
O	= 0.50
CO	= 6.00
CH_4	= 40.05
H	= 47.02
Total - - -	= 98.07 and

100 — 98.07 = 1.93, or, N = 1.93 per cent.

The following table of analyses serves to illustrate the wide range of work to which this apparatus is adapted:

GASES.	CO_2	O	CO	N	C_2H_4	CH_4	H
Flue Gas. ..... (Bituminous coal)	9.65	8.55	0.00	81.80	0.00	0.00	0.00
Hoffman Oven Gas.	1.41	0.43	6.49	0.00	2.04	36.31	53.32
Producer Gas..... (Bituminous coal)	2.50	0.30	27.00	55.30	0.40	2.50	12.00
Producer Gas..... (Anthracite coal)	2.50	0.30	27.00	57.00	0.00	1.20	12.00
Water Gas.....	4.00	0.50	45.00	2.00	0.00	3.50	45.00
Natural Gas	0.60	0.80	0.60	3.00	1.00	72.00	22.00
Coal Gas.....	0.30	0.40	7.60	2.80	4.30	36.50	48.10

The Elliott apparatus herein described is a modification of the older form, which is similar except that it is not provided with an explosion burette and has but a two-way cock at H′, and no outlet as at N′, making it difficult to expel any air caught in the horizontal capillary. This form is made full size, the burette being graduated to contain 100 cubic centimeters, and is quite largely used.

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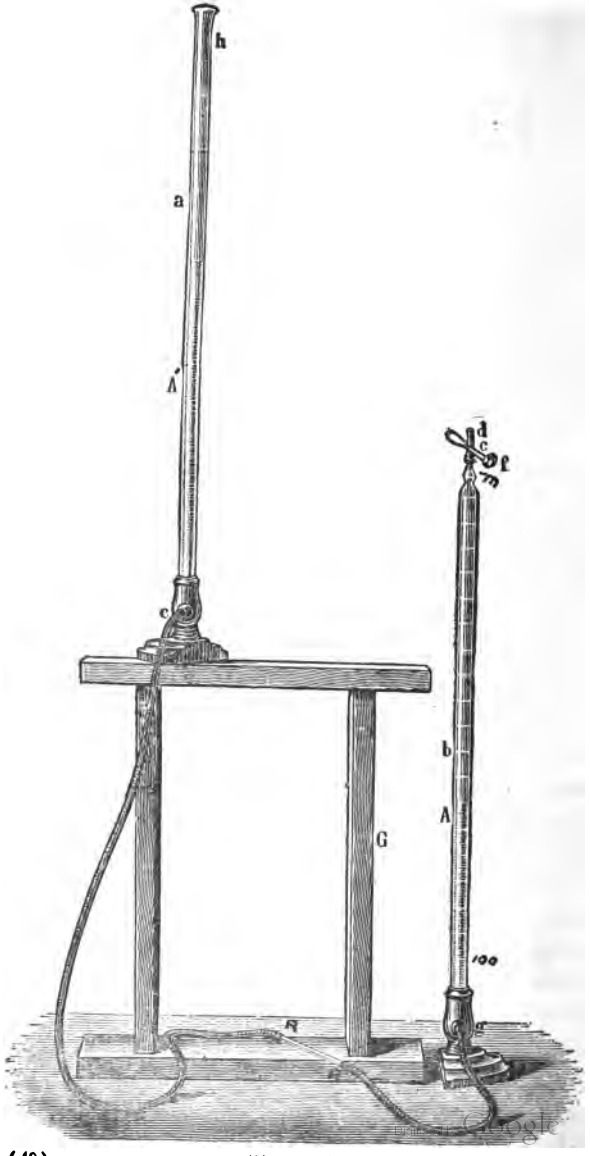
CHAPTER V.—THE HEMPEL APPARATUS.

When it is desirable to make an accurate analysis of a gas mixture in the laboratory, and when time is not an important factor, the Hempel apparatus affords a means, and is, in consequence, very largely used.

Description. The simpel gas burette, Figure 9, consists of two glass tubes, A and A′, which are connected by a thin rubber tube about 120 centimeters (about 47.24 inches) long. The ends of the tubing are simply closed over a projecting glass tip from each burette, and made fast by wrapping tightly with string. To facilitate the cleaning of the burette, the rubber tube is divided in the middle and the two ends, R R′, joined together by a piece of glass tubing. Inside the feet, the tubes A and A′ are bent at right angles and conically drawn out. They resemble, in general construction, the tubes described in the first number of these articles. The tube A is calibrated so as to contain exactly 100 cubic centimeters between the upper extremity and the lowest graduation, and is drawn out at the end to a thick walled tube *m*, while the tube A′ is widened at the end to a mouth *h* for the reception of liquids. The tube A, or measuring burette as it is termed, is supplied with or without glass stop-cocks. A piece of rubber tubing over the end *m* may be closed in a completely satisfactory manner by a Mohr pinch-cock, *f*, which is put on close to the end of the capillary. Hempel states that he found it much easier to make tight rubber tops and connections than perfectly tight glass stop-cocks, wholly aside from the fact that by giving up the glass cock the apparatus is rendered less fragile and less costly. The writer prefers the glass cocks however, and has found that



(40) FIGURE 9.

no trouble need be experienced in their use when they are kept well lubricated, as heretofore directed. If pinch-cocks are used they must be removed from the rubber tubing after using, and in the use of either pinch-cocks or glass stop-cocks occasional tests must be made to make certain that no leakage is possible. Notwithstanding the fact that readings cannot be made under the rubber tube, and that the pinch-cock cannot always be put on above the tube in exactly the same positior, no error results therefrom, since the glass tube is very small. Hempel found that differences in volume are much less than one-tenth of a cubic centimeter, a variation which, in determinations not made over mercury, may be entirely disregarded.

The graduations on the measuring burette A are divided into fifths of cubic centimeters, and the numbers run both up and down.

Operation. To briefly review the method of operation: Fill the tubes A′ and A with water which has been saturated with the gas to be examined, taking care to drive all air from the connecting rubber tube, by suitably raising or lowering the tubes; then join the burette A to the vessel containing the gas by means of a glass or rubber tube filled with water. This tube is readily filled by simply raising the level-tube A′. To fill the burette with the gas to be examined, grasp the tube A′ in the left hand, close the rubber tube at *e* by pressing it between the little finger and palm of the left hand, and pour out the water in A′. Place the level-tube A′ on the floor, and open the pinch-cock *f* on burette A. The water will now flow into the level-tube A′ and draw the gas into the burette A. As soon as A is filled with gas, close the pinch-cock *f*, disconnect A from the gas holder, and after waiting three minutes for the liquid to drain down the walls of the burette, take up the level-tube A′ by the iron feet, and by

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raising and lowering bring the water in both tubes to the same level. The gas is now under atmospheric pressure, and its volume is read off. To measure off exactly 100 cubic centimeters, bring somewhat more than 100 cubic centimeters of the gas into the burette, close the latter with the pinch-cock (or glass stop-cock), and let the water drain down for a period of three minutes. Now compress the gas to less than 100 cubic centimeters by raising the

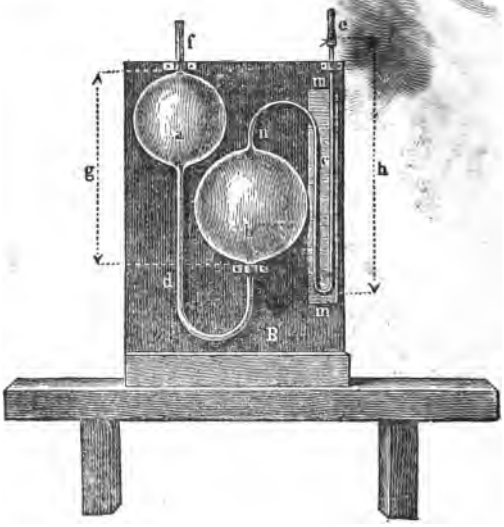

FIGURE 10.

level-tube; close the rubber tube at *g* with the thumb and first finger of the left hand, set the level-tube on the table, and, raising the burette A with the right hand to the level of the eyes, carefully open the rubber tube (held closed by the left hand), and let the water run back until the meniscus stands at the 100-cubic centimeter mark, when close rubber tube again and open the pinch-cock *f* for a moment, when the excess of gas will escape and there

remains in the burette exactly 100 cubic centimeters of the gas under atmospheric pressure. The above directions illustrate Hempel's method for obtaining a sample of exactly 100 cubic centimeters; the writer however, would suggest the method described in the first number of these articles in connection with the make-shift apparatus, by which a little more than 100 cubic centimeters of gas is drawn into the burette, then compressed to exactly 100 cubic centimeters, when the excess pressure is relieved by opening the stop-cock or pinch-cock for a moment, thereby giving just 100 cubic centimeters under atmospheric pressure.

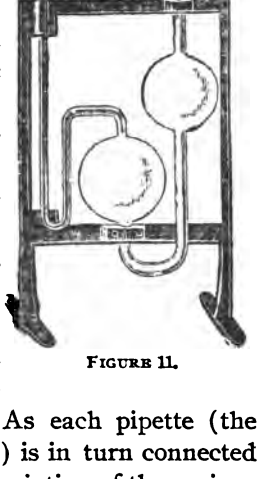

FIGURE 11.

The Hempel apparatus provides a special pipette for each reagent, so designed as to make the absorptions rapid and thorough, and yet protect the reagents from dilution or weakening by the absorption of air. As each pipette (the vessel used to contain the reagent) is in turn connected to the gas burette, the following description of the various pipettes will serve to familiarize the reader with their general operation.

The simple absorption pipette, Figure 10, consists of two large bulbs, *b* and *a*, joined by the tube *d*, and of a thick-walled glass tube, *n c*, of one-half to one millimeter internal diameter, and bent as shown in the figure. This tube will be termed the capillary tube. The bulb *a* holds about 100 cubic centimeters and *b* about 150 cubic centimeters, so that when 100 cubic centimeters of gas is brought into *b*, sufficient space for the absorbing liquid will remain. To protect the pipette from being broken and to facilitate its manipulation, it is screwed to a wooden

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or iron standard. Figures 10 and 11 show the wooden and iron supports respectively. On account of the different behavior of wood or iron and glass toward changes of temperature and atmospheric moisture, it is advisable to

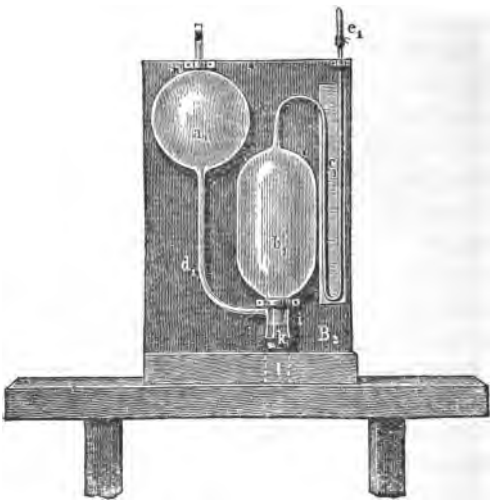

FIGURE 12.

fasten the glass at only three places by means of metal bands and sealing wax, the capillary tube being allowed to project from two to three centimeters above the frame. A short piece of rubber tubing is wired on to the free end of the capillary. The distance *h* (Figure 10) must be greater than *g*, so that it may be possible to enclose a gas between two columns of liquid in the pipette.

The simple absorption pipette for solid and liquid reagents. The only difference between this and the simple pipette is that in place of the bulb *b* (Figure 10), there is inserted the cylindrical part b_1 (Figure 12), which can be filled with solid substances through the neck *i*. A cork or rubber stopper *k*, held in place by a wire, closes the

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neck. A glass tube (Figure 13) closed at the top, and over which a rubber ring, cut from a rubber tube is drawn, makes an excellent stopper. By this arrangement only a narrow strip of rubber is exposed to the action of the reagent. See Figure 13.

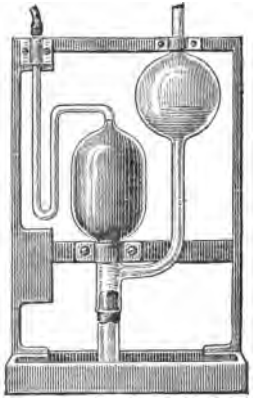

FIGURE 13.

The double absorption pipette. Reagents which are acted upon by oxygen—potassium pyrogallate, cuprous chloride, ferrous salts, etc.—cannot be kept in the aforementioned pipettes, since the reagent would, in a short time, become inactive through contact with air. The double pipette overcomes this difficulty, permitting the use of the reagents under an easily movable atmosphere which is free from oxygen, and the reagent employed may be kept completely saturated with those constituents of the gas that it does not strongly absorb, this being a great advantage. The pipette consists of the large glass bulb *a* (Figure 14), of about 150 cubic centimeters capacity, and three smaller bulbs, *b*, *c* and *d*, each containing only 100 cubic centimeters. They are connected by the bent tubes *e*, *f* and *g*, and end in the bent capillary tube *k*.

The double absorption pipette for solid and liquid reagents. The construction may be easily understood from Figure 15, and what has already been said in reference to the simple pipette for solid and liquid reagents.

To prepare the double pipettes for use, introduce the solid substance to be employed, if any, and then fill the pipette completely with the gas to be analyzed by slowly drawing the gas through. Now pour water through *m* into the bulb *d* until *g* is full. Close the rubber tube *l*

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with a pinch-cock, insert into it a thin glass tube at least one meter long, and fasten a funnel to the upper end of the latter by means of a piece of rubber tubing. Upon pouring the reagent into the funnel, the pressure due to the height of the column enables it to quickly pass through the capillary tube *k* into the bulb or cylinder *a*. The action may be hastened by gentle suction at *m*. After about 100 cubic centimeters of the reagent has been in-

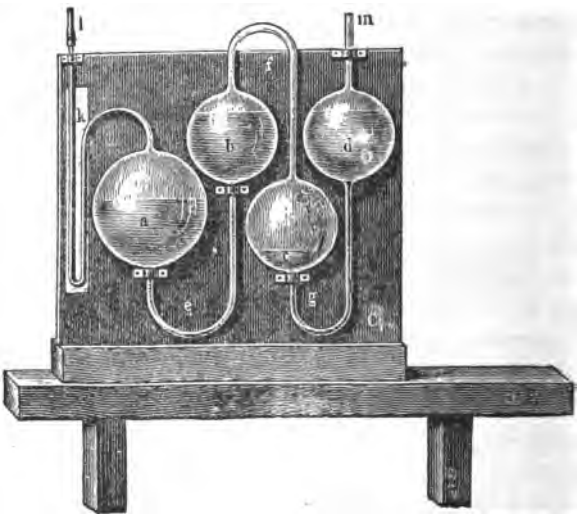

FIGURE 14.

troduced, the bulb *d* is nearly filled with water and the gas remaining in *a* is driven out through the long tube by blowing into *m*. The pipette is now closed at *l* and shaken for some time to remove from the bulb *b* the gases absorbable by the reagent. After driving out any gas bubbles which may be in *a*, suction is applied at *m* and so much gas is sucked out of the bulb *b* that the liquid in *d* will enter and fill *c*. If the water first poured in is not sufficient, more must be added from time to time.

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In pipettes thus prepared the tubes *k* and *e* and the bulb *a* are filled with the aborbent, the space from *b* to *f* with a gas free from oxygen, *c* and *g* with water, and *d* with air. While the reagent in the simple pipette may be considered to be saturated with gas only when it is kept in continual use, that in the double pipette on the contrary, remains saturated for an exceptionally long time,

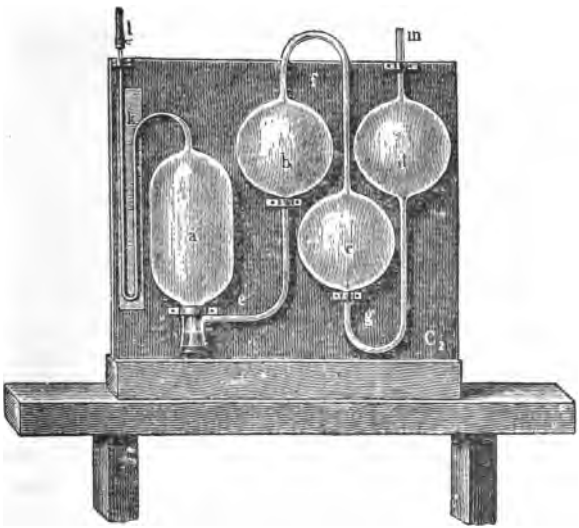

FIGURE 15.

since the diffusion must take place through the confining 100 cubic centimeters of water and through the narrow tube. The error caused by this theoretical possibility may be wholly disregarded in using the pipette. It is possible to fill the compound pipette without the aid of the long tube by manipulating so as to gradually cause the reagent to enter and then the water. When a new filling of the pipette is necessary, the reagent may easily be drawn out by means of a rubber pump.

Double absorption pipettes are now made in two sections, a construction which permits of easy and rapid filling.

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The ethylene pipette. This is a special pipette devised for use with sulphuric acid (fuming) or bromine in the absorption of ethylene and the heavy hydrocarbons or fixed illuminants. It consists of a simple pipette, having three bulbs (Figure 16), the small bulb being filled with glass beads, which afford a large absorbing surface as with the Orsat apparatus, in which glass tubes were used. With the use of sulphuric acid, it is advisable to use only that which is sufficiently concentrated, to crystallize on a slight lowering of temperature. The absorbing power of acid of this strength is 8.

One passage of the gas into the pipette is usually sufficient to effect the complete absorption of the ethylene and heavy hydrocarbons. In this reaction some sulphur dioxide (SO_2) is usually formed, and, moreover, the vapor of fuming sulphuric acid has a very high tension, so that the gas residue before being measured, must be freed from the acid vapors in the caustic potash pipette, a single passage of the gas into the pipette sufficing. To avoid having the rubber connections between the pipette and the burette attacked by the fuming sulphuric acid, the apparatus is so put together that the sulphuric acid does not quite fill the capillary of the pipette, and the connecting capillary is allowed to remain empty; the short rubber tube of the burette is also freed from liquid by means of a narrow-tipped suction pipette, any reagent remaining in the tube being first washed out with with the same pipette. If care is taken that the sulphuric acid is stopped after the absorption at the same point in the capillary at which it stood when the burette and pipette were first put together, then the small volume of air contained in the capillary tubes in the beginning causes no error in the determination of the heavy hydrocarbons or other gases, with the exception of nitrogen. In the nitrogen determination, allowance may be made for this air volume, but

as each centimeter of the empty capillary corresponds to only 0.008 cubic centimeters, this value falls below the limit of unavoidable errors. After the absorption, the rubber tube is taken off from the pipette, and the capillary and larger tube are made air-tight by closing with little glass caps, which are pushed over narrow Mohr rings placed upon the tube.

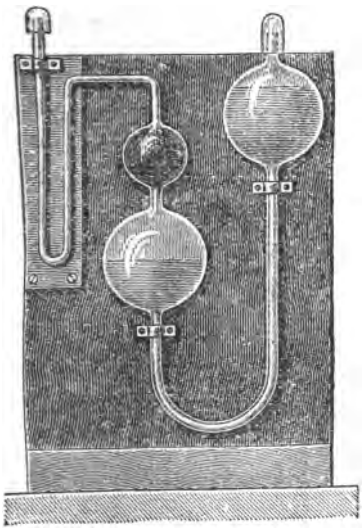

FIGURE 16.

For most purposes the bromine absorption is sufficiently accurate and far more convenient. It is also used in the pipette just described. It is not necessary to fill the pipette completely with it, being quite sufficient if a few cubic centimeters of bromine lie under water in the pipette. The bromine always remains below, there being a distinct separation of the bromine and water by reason of greater specific gravity. The water above will, however, be saturated with bromine vapor which absorbs the ethylene, etc. After this absorption, as in the case with the sulphuric acid, and as already explained in connection with the Elliott apparatus, the gas must be freed of the bromine vapor by passing it into the potassium hydroxide pipette.

The explosion pipette consists of the thick-walled explosion-bulb *a*, Figure 17, and the level-bulb *b*, which are joined together by a wrapped piece of rubber tubing. At *c* two fine platinum wires are fused into the explosion

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pipette, the ends of the wires being about two millimeters (about $^1/_{16}$-inch) apart. At *d* is a glass stop-cock, and the pipette terminates in the capillary *e*, whose end is closed by a short piece of rubber tubing and a pinch-cock. Mercury is used as the confining liquid, this tending toward greater accuracy, there being no absorption, with mercury, of the carbon dioxide formed by the combustion, as is the case when the explosion is made over water, as with the Elliott apparatus.

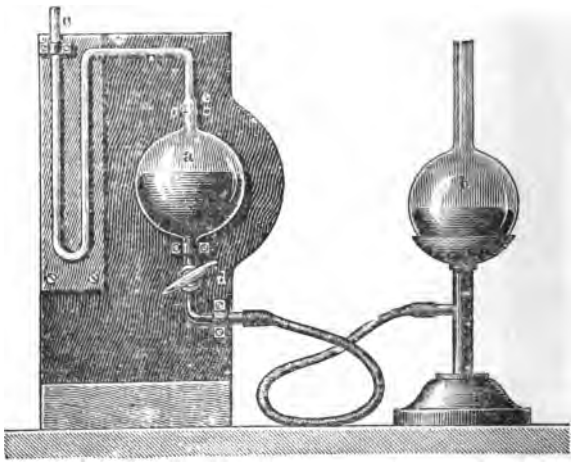

FIGURE 17.

The hydrogen generator. When one is called upon to analyze gas mixtures which do not contain sufficient combustible ingredients to make them explosive when mixed with oxygen or air, combustibility may be produced by adding pure hydrogen. This may be prepared in the special pipette, Figure 18. It is a compound absorption pipette which has two small bulbs in place of the first large bulb. Through the tube *g* a glass rod *h* is pushed up to the mouth of *e*. This rod is fastened tightly into *g*

by means of a piece of rubber tube slipped over it, and it serves to hold pieces of chemically pure zinc in the bulb *e*.

To fill the pipette it is inverted, the glass rod is taken out, and the pieces of zinc are dropped into *e*. The pipette is then closed again, placed upright, and filled with diluted sulphuric acid (1:10) by means of a funnel with a very long tube attached to the capillary *i*. The hydrogen

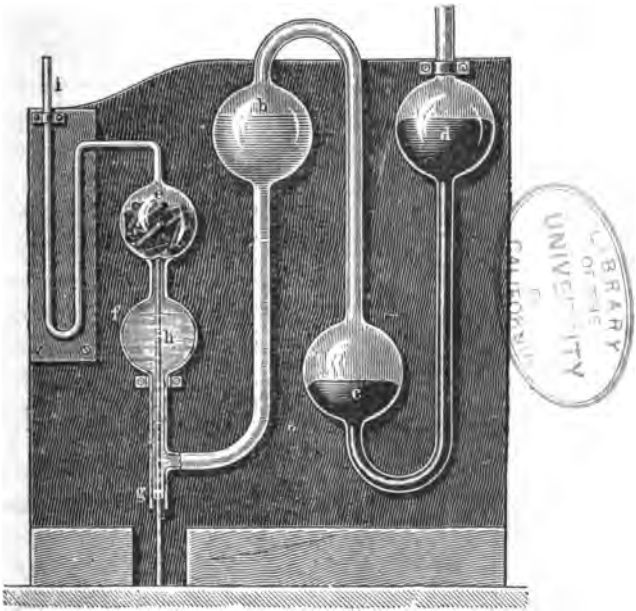

FIGURE 18.

evolved during the filling frees the sulphuric acid from any absorbed air and at the same time fills the bulbs *b* and *c*. When 100 cubic centimeters of sulphuric acid have been brought into the pipette, some mercury is poured into *d*. The pipette is closed at *i* with a piece of rubber tubing and a pinch-cock. After a short time the hydrogen produced will drive back the acid so that the

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evolution ceases; the mercury prevents the entrance of air into the apparatus, and pure hydrogen is always ready. It is advisable to force a little water into the capillary tube *i* to prevent the entrance of air at this point. A few pieces of platinum foil may be put in with the zinc to increase the evolution of hydrogen.

Explosion pipette with electrodes for the decomposition of water. A form of explosion pipette within which hydrogen and oxygen are set free by the electrical decomposition of the water contained, is shown by Figure 17. This is applicable to analyses in which the error due to the explosion being made over water will not be of consequence. Two platinum electrodes are placed in the body of the pipette, and some little distance below the line of the surface of the water when the gas is contained. These are connected by wires to a battery. Having the gas within the pipette, the battery connection is made, causing a current to pass between the electrodes through the water, separating the latter into its elementary constituents, hydrogen and oxygen. A little practice will serve to guide one as to the amount of gas required. After disconnecting the battery, connection is made with the sparking wires and induction coil, causing a spark to pass through the gas mixture and thereby igniting the gases hydrogen and oxygen resulting from the decomposition of the water. The generations of heat and pressure in connection therewith is sufficient to ignite the gas itself, which ex-

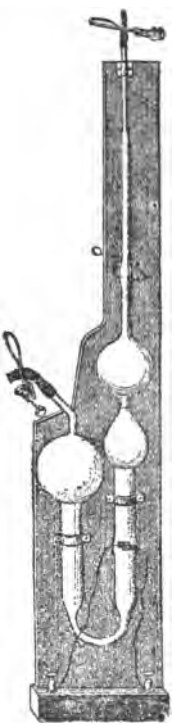

FIGURE 19.

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plodes, giving a sharp tick. No account need be taken of the amount of hydrogen and oxygen formed by the decomposition of the water, since on burning they return to the former state in the same proportion.

The combustion of the methane and hydrogen in a gas mixture may be effected without explosion, by bringing the mixture in contact with a wire heated to redness in a pipette similar to that used for solid; see Figure 20. As this method offers no advantage and requires more time for operation than the explosion pipette, a detailed description will be omitted.

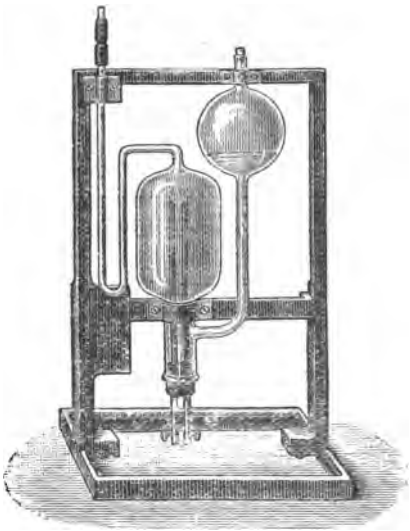

FIGURE 20.

Operation of the Hempel Apparatus. In analyzing a mixture of gases with this apparatus the gas is successively passed through the several pipettes, simple and compound, containing the reagents, after which a portion of the gas residue (portion remaining after the absorptions are complete) may be passed into the explosion pipette and burned with oxygen to determine the hydrogen, methane, and nitrogen; or, for the latter operation may be substituted fractional combustion, in which case the hydrogen is first and separately removed by palladium, after which the methane is ascertained by use of the explosion pipette.

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Manipulation of the absorption pipette. The measuring burette *b*, Figure 21, must first be filled with water previously saturated with the gas under examination.

The contents of the simple pipettes must also be saturated with the gases but slightly soluble in them. The contents of the compound pipettes remain saturated for an indefinite time owing to the enclosure of a volume of gas between two bodies of liquid.

Draw into the measuring burette *b* 100 cubic centimeters of the gas to be analyzed, method for doing which has already been described.

Note that the reagents of each pipette are brought to a position close to the upper end of the white background, generally found attached to the frame of the pipette and in the rear of the capillary tube. It would be advisable to make a mark here (see E, Figure 21), that it may serve as a guide.

Connect the measuring burette *b* containing the 100 cubic centimeters of the gas sample, to the first pipette by means of the capillary tube F and rubber tubes *d* and *i*. In making up the connections with the capillary tube F, observe all the precautions heretofore cited, seeing that no air is permitted to remain between the pinch-cocks at *d* and *i*. It is advisable to use a pinch-cock at *i* as well as at *d*. To prevent the enclosing of air, fill the rubber tube *d* above the pinch-cock with water by means of a small dropping pipette; then insert the bent capillary which becomes filled with the water displaced. By now compressing that portion of the rubber tube *i* which is above the pinch-cock, and at the same time introducing the free end of the capillary, the connection may be made without enclosing air. If, however, by some slip, there should remain any air bubbles, they will appear at the beginning as the transfer of the gas is made. In event of their not exceeding a total length of, say, 10 milli-

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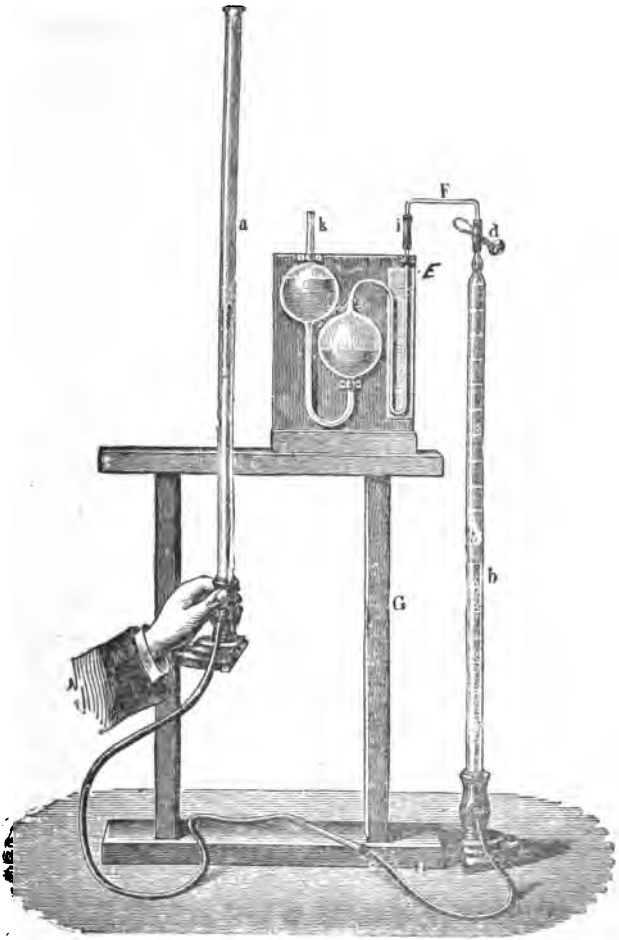

FIGURE 21.

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meters (⅜-inch), in the upright capillary tube of the pipette, they may be disregarded, since that would be indicative of but 0.03 of a cubic centimeter or of an error of $^{3}/_{100}$ of one per cent.

With the reagent in pipette at the mark E, open the pinch-cocks at *d* and *i*, having previously raised the level-tube *a*. Force the gas into the pipette, allowing a little water to pass over into the pipette also, to make certain that the entire gas volume is transferred. Close the pinch-cocks at *i* and *d* and disconnect the measuring burette without removing the capillary F from the rubber tube connections above the pinch-cock at *i*. This leaves the pipette, containing the gas, free to agitate, rendering the absorption more rapid.

After allowing sufficient time to elapse to complete the absorption of this constituent of the gas mixture, the pipette is reconnected to the measuring burette, observing the same precautions as regards the enclosing of air, and the gas transferred by lowering the level-tube.

Bring the reagent to a position in the upright capillary corresponding to the mark E, when close pinch-cocks at *i* and *d*. Measure the volume of the gas in the measuring burette under atmospheric pressure by taking the reading with the level of the liquid in both level-tube and measuring burette at the same height.

Subtract this reading from the last, and in this case (the first absorption) the reading is 100 cubic centimeters, (the amount of the gas mixture taken for a sample) and the result will be the cubic centimeters of absorption or the percentage of the constituent absorbed. The percentage in each case will be slightly in excess of the true absorption, due to the gas remaining within the capillary F, but this is hardly to be considered of consequence, although allowance may be made by measuring the capacity of the bent capillary.

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The manipulation of the compound pipettes is exactly similar, and of the pipettes for solids, the only difference lies in the case of the latter, in which the gas is exposed to the action of the solid reagent and requires no agitation as is best done to quicken the operation with a liquid reagent. By means of the Hempel pipettes, all waste is avoided, the reagents being used over and over again until exhausted.

After using, the pipettes are closed at the capillary end by the insertion of a short piece of glass rod in the rubber tube connection *i*, releasing the pinch-cock to prevent the rubber becoming set, and by closing the end of the glass tube *k* with a small cork.

It is advisable to keep an accurate account of the absorptions in cubic centimeters on the back of each pipette, so that, knowing their absorbing capacity, their full strength may be realized.

By not allowing any of the reagent to run over into the measuring burette, it will always remain clean; but should this occur, its simple construction permits of its being rinsed without trouble.

An analysis of coal gas will serve to illustrate the use of the various pipettes:

The measuring burette filled with water saturated with the gas under examination. 100 cubic centimeters of gas, measured under atmospheric pressure, admitted to the measuring burette.

The gas transferred from the measuring burette to the first pipette, a simple pipette containing potassium hydroxide. After thoroughly agitating the gas with the reagent, it was drawn back into the burette. After a lapse of three minutes to allow the burette walls to drain, the volume was measured and found to be 99.6 cubic centimeters. This, subtracted from 100 cubic centimeters, gave the percentage of carbon dioxide:

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100 — 99.6 = 0.4, or CO_2 = $^1/_{10}$ of 1. per cent.

Gas was passed into the second pipette, a special pipette containing bromine. After agitating, the gas was returned to the measuring burette, and then, previous to measuring, passed into the first or potassium hydroxide pipette, to remove the bromine vapors. Returned to measuring burette, and after a lapse of three minutes gas volume measured and found to be 95.3 cubic centimeters. This, subtracted from the last reading, 99.6, gave the percentage of fixed illuminants or heavy hydrocarbons:

99.6 — 95.3 = 4.3, or C_2H_4 = 4.3 per cent.

Instead of employing bromine, fuming sulphuric acid might have been used for the absorption of the heavy hydrocarbons.

The gas was passed into the third pipette, a compound pipette containing potassium pyrogallate. After agitating, the gas was returned to the measuring burette, and after a lapse of three minutes, gas volume measured and found to be 94.8 cubic centimeters. This, subtracted from the last reading, 95.3 cubic centimeters, gave the percentage of oxygen:

95.3 — 94.8 = 0.5, or O = ½ of 1 per cent.

Instead of employing potassium pyrogallate, phosphorus might have been used for the absorption of oxygen.

The gas was passed into the fourth pipette, a compound pipette containing ammoniacal cuprous chloride. After thoroughly agitating, and allowing to remain in contact with the reagent some three minutes, the gas was returned to the measuring burette, and after a lapse of three minutes gas volume measured, and found to 87.1 cubic centimeters. This, subtracted from the last reading, 94.8 cubic centimeters, gave the percentage of carbon monoxide:

94.8 — 87.1 = 7.7, or CO = 7.7 per cent.

Instead of employing ammoniacal cuprous chloride,

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cuprous chloride might have been used for the absorption of carbon monoxide, the former being required only when palladium is used for the absorption of hydrogen.

The 87.1 cubic centimeters of gas now remaining, termed the gas residue, transferred to the ammoniacal cuprous chloride pipette, which served simply as a holder. The measuring burette thoroughly rinsed out with hydrochloric acid and water and refilled with water saturated with air.

A little of the gas residue (from 12 to 20 cubic centimeters) was drawn into the measuring burette, and after a lapse of three minutes gas volume measured, and found to be 14.5 cubic centimeters. This was transferred to the explosion pipette, after having added some 15 cubic centimeters of air, and oxygen sufficient to bring the total volume up to 100 cubic centimeters. In making the transfer from the measuring burette, care was taken to have a little water pass over, and the rubber connecting piece was closed by a strong pinch-cock so as to confine the water within the pipette capillary. A piece of glass rod was also slipped into the open end of the rubber tube above the pinch-cock on the measuring burette being disconnected. The pipette was then thoroughly agitated to mix the gas, oxygen and air, the glass stop-cock closed, and by connecting to the induction coil and battery a spark was passed causing the mixture to explode. The glass stop-cock at once opened, and the gas transferred to the measuring burette, where, after a lapse of three minutes, gas volume was measured and found to be 76.05 cubic centimeters. This, subtracted from the total amount before the explosion, 100 cubic centimeters, the contraction:

$$100 - 76.05 = 23.95 \text{ cubic centimeters contraction.}$$

The gas was now transferred to the first pipette, containing potassium hydroxide, and, after agitation, returned to the measuring burette, where, after a lapse of three

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minutes, the gas volume was measured and found to be 70.15 cubic centimeters. This, subtracted from the former reading, 76.05 cubic centimeters, gave the carbon dioxide formed, which is equal to the methane:

$76.05 - 70.15 = 5.90$ cubic centimeters = methane.

The gas was now transferred to the potassium pyrogallate pipette, to make certain there had been oxygen in excess,* and, after agitation, returned to the measuring burette. After a lapse of three minutes, the gas volume was measured and indicated an absorption of oxygen.

We now have all the data for the computation of the hydrogen, methane, and nitrogen.

Methane in portion of gas residue exploded, 14.5 cubic centimeters equaled 5.9 cubic centimeters.

By proportion, the methane in the total gas residue, 87.1 cubic centimeters, would equal, therefore:

$$87.1 : 14.5 :: X : 5.9;$$

$$\text{or, } X = 35.4; \text{ or, } CH_4 = 35.4 \text{ per cent.}$$

Hydrogen in portion of gas residue exploded, 14.5 cubic centimeters, equaled 8.09 cubic centimeters, since

$$H = \frac{2C - 4D}{3}$$

in which H = hydrogen
C = contraction
D = methane
the contraction = 23.95
the methane = 5.9

hence by substituting

$$H = \frac{2(23.95) - 4(5.9)}{3} = 8.09$$

and for the total gas residue the hydrogen is found by proportion

$$87.1 : 14.5 :: Y : 8.09;$$

$$\text{or, } Y = 48.5; \text{ or, } H = 48.5 \text{ per cent.}$$

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*This is a needless precaution in our case since oxygen was added in excess.

Tabulating the amounts found:

$$\begin{aligned} CO_2 &= 0.4 \\ C_2H_4 &= 4.3 \\ O &= 0.5 \\ CO &= 7.7 \\ H &= 48.5 \\ CH_4 &= 35.4 \\ &\overline{96.8} \end{aligned}$$

hence the nitrogen found by difference is
100 — 96.8 = 3.2 cubic centimeters; or, N = 3.2 per cent.

SPECIAL SCHEMES.

The Fractional Combustion of Hydrogen. By use of the apparatus shown in Figure 20 the amount of hydrogen present in a mixture consisting of hydrogen, nitrogen and methane may be obtained by direct absorption, the methane being subsequently determined by ignition in the explosion pipette, and the nitrogen by difference. In Figure 20, *a* and *b* are the level-tube and measuring burette respectively; the latter being connected by means of the capillary E to a special tube H, of about four millimeters ($^5/_{32}$-inch) internal diameter, and some 20 centimeters (about 8 inches) in length, containing about four grains of palladium sponge. The palladium tube H is connected by another capillary tube, E′, to a simple pipette which may contain water, or, if preferable, potassium hydroxide, by use of the latter avoiding the necessity of an extra pipette. The pipette serves as a receiver. The beaker, in which is placed the tube H, is nearly filled with water, the temperature of which may be maintained at such a degree as to make possible only the absorption of the hydrogen.

Operation. After completing the removal of all the absorbable constituents of the gas mixture other than hydrogen, and with the gas residue in the *ammoniacal*

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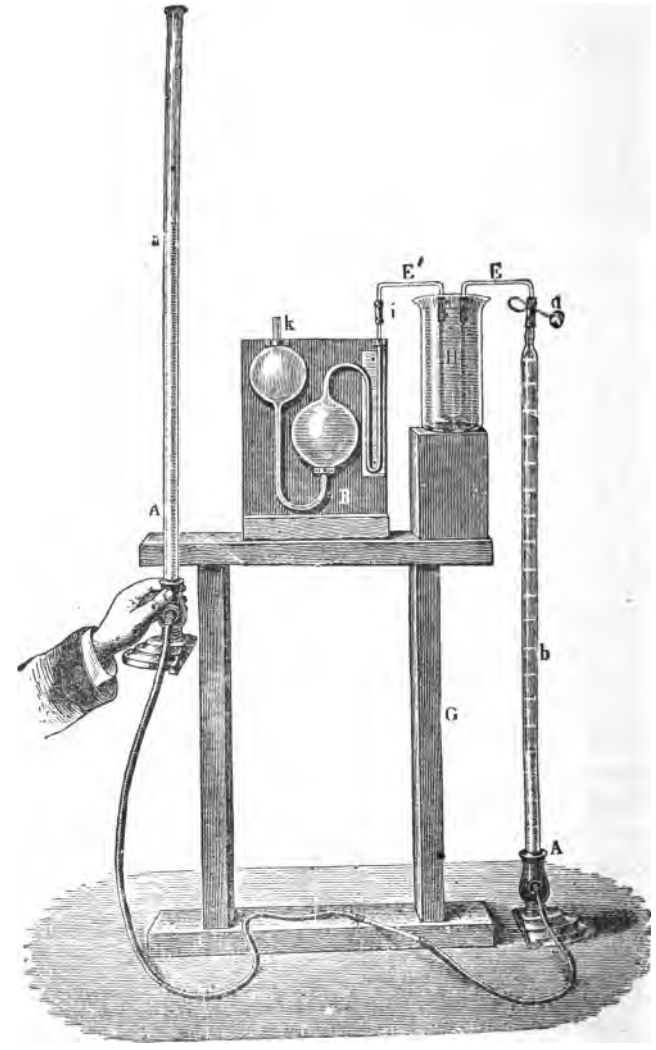

FIGURE 22.

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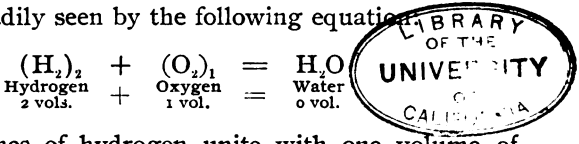
cuprous chloride pipette, draw into the measuring burette some of the gas residue, and, after waiting three minutes for drainage, measure. Join the burette to the palladium tube and receiving pipette B by means of the capillaries, having previously drawn the liquid in the pipette to the mark on the capillary stem, as heretofore directed in connection with the use of the Hempel pipette. Bring the temperature of the water in the beaker to about 95° C., not allowing it to exceed 100° C., nor fall below 90° C. Open the pinch-cock *d*, and by raising the level-tube *a*, force the gas through the capillary and palladium tubes and into the pipette. Return the gas to the measuring burette and repeat the transfer a couple of times. Replace the hot water by fresh water of about the temperature of the room, and thoroughly cool the gas by leading it back and forth through the palladium tube a few times. By now measuring the gas volume and thus determining the contraction, taking account of the air contained by the capillary and the palladium tubes, the amount of hydrogen in the sample of gas residue becomes known, since in the presence of the palladium, all of the hydrogen unites with such oxygen (afforded by the air added) as is required for chemical union. The product being water, two-thirds of the contraction equals the volume of hydrogen, as is readily seen by the following equation:



$$\underset{\text{Hydrogen 2 vols.}}{(H_2)_2} + \underset{\text{Oxygen 1 vol.}}{(O_2)_1} = \underset{\text{Water 0 vol.}}{H_2O}$$

Two volumes of hydrogen unite with one volume of oxygen to form water possessing no appreciable volume.

Having determined the hydrogen by the palladium absorption, draw into the measuring burette another portion of the gas residue from the *ammoniacal* cuprous chloride pipette; wait three minutes for drainage and measure the volume. Pass this into the explosion pipette

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and then add the requisite quantity of air and pure hydrogen; the latter is generated by means of the hydrogen pipette already described.* The gases are now thoroughly mixed and ignited by means of a spark. The contraction, due to combustion, is measured, and the carbon dioxide formed is absorbed by passing the products of combustion into the potassium hydroxide pipette. The absorption is then measured.

We now have sufficient data for the computation of the constituents of the gas residue.

The total contraction produced corresponds to:

1. The hydrogen present in the original gas (this is ascertained by the palladium absorption) plus one-half its volume of oxygen, the quantity requisite for complete combustion.

2. The measured quantity of hydrogen added, plus one-half its volume of oxygen.

3. The methane present (equal to the carbon dioxide formed, as measured by the potassium hydroxide absorption) plus two volumes of oxygen requisite for its combustion.

Knowing the percentages of both the hydrogen and the methane, we need only be concerned as regards the nitrogen. Its volume or percentage is readily found by adding the percentages of all the other constituents and subtracting the total from 100, the result being the percentage of nitrogen.

It is not absolutely necessary to measure the carbon dioxide formed to determine the methane; simply ignite the mixture of gases in the explosion burette, and then, without measuring the contraction, transfer to the potassium hydroxide pipette for the absorption of the carbon dioxide formed; after which, measure the volume to ascer-

*Oxygen may be used as heretofore should it be preferable.

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tain the total contraction, which will equal the sum of the contractions 1, 2 and 3.

Since the contractions 1 and 2 are known by taking their sum from the total contraction (the sum of 1, 2 and 3), the contraction due to the combustion of the methane becomes known, and thus the volume and percentage of methane, it being one-third of contraction 3. Thus:

$$\text{Total contraction} = C = 1 + 2 + 3$$
$$\text{then } C - (1 + 2) = 3$$

Now methane—CH_4—in burning unites with two volumes of oxygen; thus:

$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{(O_2)_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{Water.}}{(H_2O)_2}$$

and the carbon dioxide being absorbed previous to measuring the contraction, gives a contraction due to methane of three volumes for each volume burned, hence one-third of the contraction (3) equals the volume of methane.

It is not even necessary to trouble to make the absorption of the carbon dioxide formed with potassium hydroxide, since in this case the volume of carbon dioxide formed by the combustion, remaining unabsorbed, lessens the contraction by one volume for every volume of methane burned; hence the volume of methane will in this case become one-half of the contraction due to the combustion of the methane.

Conditions to be observed in connection with the absorption of hydrogen by means of palladium:

In a gas mixture, the carbon dioxide, heavy hydrocarbons, oxygen, carbon monoxide, etc., must first be as completely removed as is possible by absorption with reagents. For the absorption of carbon monoxide only *ammoniacal* cuprous chloride may be used, since the acid fumes of the cuprous chloride would tend to unite with the oxygen of the palladium oxide more readily than

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hydrogen, and in burning not develop sufficient heat to make possible the occlusion of the hydrogen. On the other hand, traces of ammonia do not interfere. Carbon monoxide or large quantities of benzole vapor or vapor of alcohol do interfere, owing, as in the case of hydrochloric acid, to their greater affinity for palladium oxide, and, in consequence, every care should be exercised to remove them as far as possible.

Palladium black is even stronger in its action than oxydized palladium sponge. It is made by reducing palladium chloride with alcohol in a strongly alkaline solution. It is probably a mixture of metallic palladium with palladium oxide.

The palladium may be regenerated by plunging the tube into hot water and passing a current of dry air through it. The palladium should always be kept as dry as possible.

The Absorption of Oxygen by Phosphorus. The employment of moist phosphorus as an absorbent of oxygen is by far preferable to the use of potassium pyrogallate, but this method is not universally applicable. The absorption is carried on in a simple pipette for solids, thin sticks of phosphorus being inserted in the bulbed portion and surrounded by water, which recedes on the gas being forced in, thus affording a fresh, bright surface of phosphorus for each absorption. The moist surface of the phosphorus rapidly absorbs the oxygen, forming phosphoric and phosphorus acid, both of which are dissolved by the water present. The temperature of the pipette should be held at from 18° to 20° C., (64° to 68° F.). About ten minutes should be allowed this absorption.

The following conditions should be observed in connection with the employment of phosphorus:

The oxygen in the gas should not exceed 50 per cent.

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The gas should be free from ammonia, ethylene and all hydrocarbons, vapor of alcohol, ether, and etherial oils.

It is owing to the fact that phosphorus is not acted upon by oxygen except the latter is diluted with other gas, that one should not have it present in greater quantity than 50 per cent. In gases rich in oxygen it is easy to dilute with nitrogen to permit of the absorption.

During the reaction, a bright glowing of the phosphorus takes place, and the termination of the oxidation is sharply shown by its disappearance on the exhaustion of the oxygen. The glow is only visible in a dark room. The phosphorus may be repeatedly used but should be protected from the light when not in use. The confining water surrounding the phosphorus should be renewed occasionally to prevent saturation and allow of the products of combustion or oxidation being readily absorbed, and in this way keeping the surface of the phosphorus always bright and active.

Scheme for the Analysis of Coal Gas by which the traces of carbon monoxide remaining from the cuprous chloride absorption, and any ethane present, may be determined.

The writer has found, that even with the exercise of considerable care, there remains some carbon monoxide after the cuprous chloride absorption; and further, that there is generally present in the gas residue traces, at least, of ethane (C_2H_6). He has accordingly arranged the following method for the analysis of a gas mixture, which provides a means for the complete determination of carbon monoxide and ethane. The gas mixture may contain benzene, or benzole vapor, C_6H_6; carbon dioxide, CO_2; heavy hydrocarbons or fixed illuminants, C_2H_4; oxygen, O; carbon monoxide, CO; hydrogen, H; methane, CH_4; ethane, C_2H_6; and nitrogen, N.

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In making use of this scheme the following order of analysis should be observed:

1. Benzene or benzole vapors (C_6H_6), absorbed by one cubic centimeter of alcohol in mercury pipette; after measuring the contraction agitate the gas with one cubic centimeter of water to remove alcoholic vapors.

2. Carbon dioxide (CO_2), absorbed by potassium hydroxide. The absorption is nearly instantaneous, one passage of the gas into the pipette generally sufficing.

3. Heavy hydrocarbons or fixed illuminants, consisting principally of ethylene (C_2H_4), absorbed by an aqueous solution of bromine. Fuming sulphuric acid gives a slightly greater absorption, but bromine is far more convenient and sufficiently accurate for most purposes. Time required for this absorption, three minutes.

4. Oxygen (O), absorbed by phosphorus. Time, ten minutes. Potassium pyrogallate may be used, but the first offers a decidedly more elegant method. Time with potassium pyrogallate, three minutes.

5. Carbon monoxide (CO), absorbed by a solution of cuprous chloride. An alkaline or ammoniacal solution of cuprous chloride must be used, since the absorption of hydrogen is to be by means of palladium, which would become inactive in the presence of hydrochloric acid vapors. In making the cuprous chloride absorption, it is advisable to employ two pipettes,* one containing a solution which has been used a number of times, and the other comparatively fresh. By passing the gas into the first and agitating therein some two or three minutes, and thus removing the greater part of the carbon monoxide, and then completing the absorption by a passage into the second pipette, retaining there some three minutes. This precaution is taken owing to the fact that the affinity of carbon monoxide for cuprous chloride is but slight, and

*Queen & Co., of Philadelphia, construct an apparatus for this purpose, consisting of three parts, which is very convenient.

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the resulting union is, in consequence, rather unstable. Even by the use of two pipettes traces of carbon monoxide remain.

The residulal gas may now consist of

$$H + CO \text{ (traces remaining unabsorbed by cuprous chloride solution)} + CH_4 + C_2H_6 + N.$$

This residual gas is retained in the cuprous chloride pipette, a portion, say 20 cubic centimeters, being taken for the palladium absorption. In the palladium reaction already described (the 20 cubic centimeters of residual gas is simply passed, together with the air added, over palladium), are removed the hydrogen and remaining traces of carbon monoxide.

The combustion of the two is represented by the equations:

$$H_2 + (O_2)_{\frac{1}{2}} = H_2O \qquad (1)$$

$$CO + (O_2)_{\frac{1}{2}} = CO_2 \qquad (2)$$

In equation 1, one volume of hydrogen uniting with one-half volume of oxygen, condenses to water. The contraction is therefore one and one-half volumes, which is one and one-half times the hydrogen burned, or 1½ H.

In equation 2, one volume of carbon monoxide uniting with one-half volume of oxygen, contracts to one volume of carbon dioxide. The contraction is therefore one-half the carbon monoxide burned, or ½ CO. In this combustion there is formed one volume of carbon dioxide for each volume of carbon monoxide burned, or $CO = CO_2$. This affords a means of determining the amount of carbon monoxide, since the carbon dioxide may be absorbed by potassium hydroxide.

Collecting, we have for the total contraction due to the palladium combustion:

$C_1 = 1\frac{1}{2}\ H + \frac{1}{2}\ CO$, (3) and

$D_1 = CO = CO_2$, (4) in which

C_1 = the contraction due to palladium combustion,

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D_1 = carbon dioxide formed by palladium combustion, substituting in equation 3 the value of CO in equation 4

$$C_1 = 1\tfrac{1}{2}\,H + \tfrac{1}{2}\,D_1 \quad (5)$$

and by simple transposition

$$H = \frac{2\,C_1 - D_1}{3} \quad (6)$$

The operation thus far is then to pass the sample of residual gas, to which has been added air, over palladium, causing the H and CO to be burned. The products of the combustion are then brought back and the volume measured, showing the contraction, which is designated C_1 in the above formulas. The gas is then passed into the potassium hydroxide pipette for the absorption of the carbon dioxide (formed by the combustion of the carbon monoxide). The gas is returned to the measuring burette and the contraction due to the carbon monoxide absorption measured; this equals D_1 in the above formulas. We now know the hydrogen and the carbon monoxide of the residual gas sample.

Another portion of the residual gas is now drawn from the cuprous chloride pipette and measured—say about 15 cubic centimeters—and to this is added about 80 cubic centimeters of air, enough to make a total of nearly 100 cubic centimeters. The mixture is transferred to the explosion burette and well mixed. It is then exploded over mercury. The resulting contraction we will call C— and is due to the following reactions:

The carbon monoxide burning to carbon dioxide

(*a*) $CO + (O_2)_{\frac{1}{2}} = CO_2$ Contraction = $\frac{1}{2}$ CO

The volume of carbon dioxide formed equals the volume of carbon monoxide burned; or, $CO_2 = CO$.

The methane burning to carbon dioxide and water

(*b*) $CH_4 + (O_2)_2 = CO_2 + (H_2O)_2$

Contraction = 2 CH_4

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The volume of carbon dioxide formed equals the volume of the methane burned; or, $CO_2 = CH_4$

The ethane burning to carbon dioxide and water

$$(c) \quad C_2H_6 + (O_2)_{3\frac{1}{2}} = (CO_2)_2 + (H_2O)_3$$

Contraction $= 2\frac{1}{2}\ C_2H_6$

The volume of carbon dioxide formed equals twice the volume of ethane burned; or, $CO_2 = 2C_2H_6$

The hydrogen burning to water

$$(d) \quad H_2 + (O_2)_{\frac{1}{2}} = H_2O \qquad \text{Contraction} = 1\frac{1}{2}H$$

The total contractions (C) resulting from the combustion of residual gas in the explosion pipette is then the sum of the contractions resulting from the reactions expressed by equations *a*, *b*, *c*, and *d*; or,

$$C = \tfrac{1}{2}CO + 2\,CH_4 + 2\tfrac{1}{2}C_2H_6 + 1\tfrac{1}{2}H \qquad (7)$$

The total volume of carbon dioxide (we will designate this D) formed by the combustion of residual gas in the explosion pipette, would equal from the equations *a*, *b*, *c*, *d*

$$D = CO + CH_4 + 2\,C_2H_6 \qquad (8)$$

The procedure is then to ignite the sample of residual gas in the explosion pipette, then returning to the measuring burette to determine the contraction (C), then transferring the gas to the potassium hydroxide pipette to absorb the carbon dioxide formed, afterwards measuring in the burette the volume of absorption (D).

Let us call

$$C - C_1 = E = (\tfrac{1}{2}CO + 2CH_4 + 2\tfrac{1}{2}C_2H_6 + 1\tfrac{1}{2}H) - (1\tfrac{1}{2}H + \tfrac{1}{2}CO) = 2CH_4 + 2\tfrac{1}{2}\,C_2H_6 \qquad (9)$$

Let us call

$$D - D_1 = F = (CO + CH_4 + 2C_2H_6) - (CO) = CH_4 + 2C_2H_6 \qquad (10)$$

Then multiplying F by 2 and subtracting E we have

$$2F - E = (2CH_4 + 4C_2H_6) - (2CH_4 + 2\tfrac{1}{2}C_2H_6) = 1\tfrac{1}{2}C_2H_6 \qquad (11)$$

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$$\text{or,} \quad C_2H_6 = \frac{4F - 2E}{3} \qquad (12)$$

and further, we have from equation 10

$$CH_4 = F - 2C_2H_6 \qquad (13)$$

The nitrogen is now found by difference making all the constituents of the residual gas known.

One fact to be noticed is that F or $D - D_1$ cannot, under any circumstances, be less than $\frac{1}{2}E$ or $\frac{1}{2}(C - C_1)$, since, if in equations

$(F = CH_4 + 2C_2H_6)$ and $(E = 2CH_4 + 2\frac{1}{2}C_2H_6)$

$$CH_4 = O, \text{ then } F = 2C_2H_6 = \tfrac{4}{5}E; \qquad (14)$$

or, if on the other hand,

$$C_2H_6 = O, \text{ then } F = CH_4 = \tfrac{1}{2}E \qquad (15)$$

Summing up, the residual gas may consist of

$$H + CO + CH_4 + C_2H_6 + N$$

By the palladium combustion

$$H = \frac{2C_1 - D_1}{3}$$

in which C_1 = the contraction due to the combustion of the hydrogen and carbon monoxide and D_1 = the carbon dioxide resulting = the carbon monoxide burned.

By the explosion over mercury

$$C_2H_6 = \frac{4F - 2E}{3}, \text{ and}$$

$$CH_4 = F - 2C_2H_6$$

in which

$F = D - D_1$ = the difference between the volumes of carbon dioxide formed by the explosion over mercury (D) and the palladium combustion (D_1).

$E = C - C_1$ = the difference between the contraction from the explosion and palladium combustion.

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CHAPTER VI.—MEASUREMENT OF GASES.

CORRECTION FOR PRESSURE, TEMPERATURE AND VAPOR TENSION.

Owing to the fact that the volume of a gas varies with change of pressure and temperature, it is necessary to reduce volumes measured under different conditions to some set standard in order that a true comparison may be arrived at. Universal custom has determined this standard as 760 millimeters (29.92158 inches) of mercury for pressure, and 0° C. (32° F.), for temperature; hence by reducing to these conditions, gases of similar composition will always be of equal mass or weight per unit of volume or of equal volume per unit of mass or weight. With this understanding, we may speak of one liter of a certain gas as always having the same mass or weight, and likewise of one gram as always having the same volume, knowing that under like conditions of pressure and temperature there will exist a constant relation between volume and mass.

The pressure acting upon a gas is generally measured in millimeters or inches of mercury: that is, in terms of the height of a column of mercury which it sustains; thus the atmospheric pressure is read from a barometer as so many millimeters or inches of mercury.

In determining the volume of a gas, therefore, it is necessary to consider the conditions under which it is measured. If in an open vessel or in a vessel over a liquid, as mercury or water, in which the level of the liquid is the same inside as it is outside the vessel, then a reading of the barometer, giving the atmospheric pressure, likewise gives the pressure acting upon the gas.

To measure a gas under atmospheric pressure it is only

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necessary therefore, to confine it in a vessel over a liquid by means of a level tube, and adjust the tube so as to bring the level of the liquid both inside the vessel and in the level tube to the same height, for should the level of the liquid within the vessel be higher than in the tube, the gas will be under diminished pressure, and if, on the other hand, it is lower than in the tube, it will be under a pressure greater than atmospheric, due to the weight of the column of liquid above its level. In Figure 23, if mercury be used for the confining liquid in a level-tube A′ open to the atmosphere, and a measuring burette A closed at the upper end by a pinch-cock, then it is evident that with the levels of the mercury at *a′* and *a* in the level-tube and measuring burette respectively, the gas enclosed in the latter above the mercury is not exerting as great a pressure as is the atmosphere on the liquid at the open end of the level-tube where the level is the lowest. The

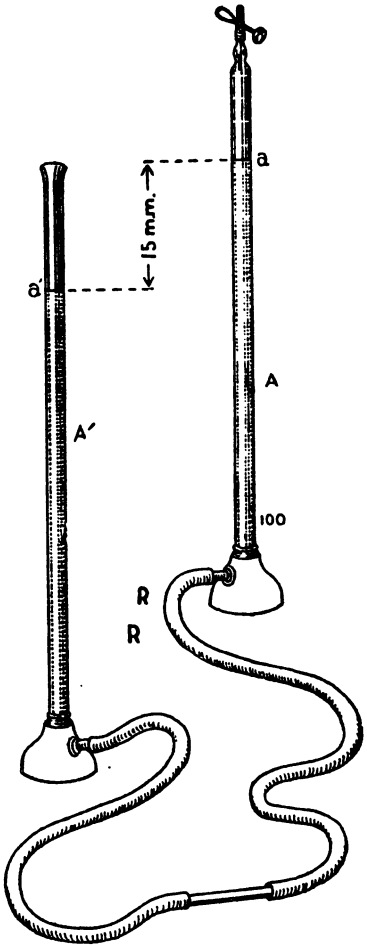

FIGURE 23.

pressure upon the gas is equal in this case to the atmospheric less 15 millimeters, the distance between the levels, which equals, with an atmospheric pressure of 760 millimeters, 745 millimeters of mercury as actual pressure.

Were the case reversed, that is, were the level a 15 millimeters lower than the level a', then the pressure on the gas would equal 760 + 15, or 775 millimeters of mercury.

If water is employed as the confining liquid instead of mercury, it will be necessary to determine the pressure in terms of mercury in order to make use of the barometer and standard conditions. Mercury has a specific gravity of 13.6; that is, the weight of a given volume of water is but $1/13.6$ part of the weight of an equal volume of mercury. In the foregoing example, had the liquid been water, with the same pressure acting upon the gas, there would have been a difference of level of about 204 millimeters of water, which, divided by 13.6 would give the 15 millimeters of mercury.

Influence of Pressure on Volume. What is known as Boyle's law states that *the volume of a perfect gas varies inversely as the pressure it supports;* that is, the greater the pressure the less the volume. The following example will serve to illustrate this:

A volume of ethylene, C_2H_4, measures two liters under a pressure of 750 millimeters of mercury. What would its volume be under standard conditions of pressure, temperature being neglected?

Standard pressure is 760 millimeters of mercury; consequently we are to determine the volume under an increased pressure, which, by the law of Boyle, will give us a smaller volume. Thus:

760 mm. : 750 mm. :: 2 litres : X (the required volume)

$$\text{or, } 2 \times \frac{750}{760} = X; \text{ or, } X = 1.9 \text{ liters;}$$

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that is, the volume under standard conditions of pressure will be 1.9 liters. Conversely:

A volume of ethylene, C_2H_4, measures 1.9 liters under a pressure of 760 millimeters of mercury. What would its volume be under a pressure of 750 millimeters, temperature being neglected?

It is here required to ascertain what the volume of a gas, measured under standard conditions of pressure, would be under a given decreased pressure, which, by the law, will give a greater volume. Thus:

750 mm. : 760 mm. :: 1.9 (liters) : X (required volume)

$$\text{or, } 1.9 \times \frac{760}{750} = X; \text{ or, } X = 2 \text{ liters.}$$

The above operations may be stated more briefly in the following rule:

Multiply the volume actually measured by a fraction whose numerator and denominator will be the absolute pressures, the greater of which will be the denominator or numerator according as the volume is to be decreased or increased, which may be seen by an inspection of the problem and an understanding of Boyle's law.

Influence of Temperature on Volume. Actual experiment has proven that all gases have the same coefficient of expansion by heat. In the centigrade scale the coefficient of expansion per degree is 0.003665, or, expressed in fractional form, $1/_{273}$; that is, the pressure being constant, the volume of a perfect gas increases $1/_{273}$ of its volume at 0° C., for every increase in temperature of 1° C., and in Fahrenheit units 0.002036, or $1/_{491.2}$ of its volume at 32° F., for every increase of 1° F. Likewise it decreases for each negative degree.

It follows, then, that the volume at

1° C. = vol. at 0° C. + $\frac{1}{273}$ (vol. at 0° C.) = $\frac{274}{273}$ (vol. at 0° C.)

2° C. = vol. at 0° C. + $\frac{2}{273}$ (vol. at 0° C.) = $\frac{275}{273}$ (vol. at 0° C.)

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3° C. = vol. at o° C. + $\frac{3}{273}$ (vol. at o° C.) = $\frac{273}{273}$ (vol. at o° C.)

t° C. = vol. at o° C. + $\frac{t}{273}$ (vol. at o° C.) = $\frac{273}{273}^{\text{plus t}}$ (vol. at o° C.)

and the volume at

— 1° C. = vol. at o° C. — $\frac{1}{273}$ (vol. at o° C.) = $\frac{272}{273}$ (vol. at o° C.)

— 2° C. = vol. at o° C. — $\frac{2}{273}$ (vol. at o° C.) = $\frac{271}{273}$ (vol. at o° C.)

— 3° C. = vol. at o° C. — $\frac{3}{273}$ (vol. at o° C.) = $\frac{270}{273}$ (vol. at o° C.)

and at

— 273° = vol. at o° C — $\frac{273}{273}$ (vol. at o° C.) = $\frac{0}{273}$ (vol. at o° C.)

that is, at — 273°, by the law, the gas would entirely disappear or be of no volume, which would be impossible. To account for this apparent discrepancy in the law governing the effect of temperature on perfect gases, we find that as gases approach the temperature of liquification, their properties change from those of a perfect gas and thus they deviate from the law. In order to facilitate computation, however, the temperature of —273° C. is considered as absolute zero. To obtain absolute temperature, therefore, *add 273° to the readings of the Centigrade thermometer, or 459.2° (= 491.2 — 32)—generally taken as 460°—to the readings of the Fahrenheit thermometer.*

From the foregoing it is readily seen that if a volume of gas measured 273 cubic centimeters at o° C., (which is 273° C. absolute temperature), and was raised one degree, bringing the absolute temperature to 274° C., the volume would be increased $\frac{1}{273}$ of the volume at o° C., or the volume would become 273 + 1 = 274 cubic centimeters; and similarly, if raised 5° C., the volume would become 273 + 5 = 278 cubic centimeters. We may therefore restate the law, known as that of Charles, as follows:

The volume of a gas varies directly as its absolute temperature; that is, the greater the temperature, the greater the volume, and the less the temperature, the less the volume.

The following example will serve to illustrate the use of this law:

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A volume of ethylene, C_2H_4, measures two liters at a temperature of 21° C. (69.8° F.). What would the volume be under standard conditions of temperature, pressure being neglected?

Standard temperature is 0° C.; consequently we are to determine the volume under decreased temperature, which by the above law, will give a decreased volume. Thus:

Reducing all temperatures to absolute

$$21^\circ \text{ C.} = 273 + 21 = 294^\circ \text{ C. absolute}$$

$$0^\circ \text{ C.} = 273^\circ \text{ C. absolute; then,}$$

$$294^\circ \text{ C.} : 273^\circ \text{ C.} :: 2 \text{ (liters)} : X \text{ (required volume)}$$

$$\text{or, } 2 \times \frac{273}{294} = X; \text{ or, } X = 1.8 \text{ liters;}$$

that is, the volume under standard conditions of temperature will be 1.8 liters. Conversely:

A volume of ethylene, C_2H_4, measures 1.8 liters at a temperature of 0° C., what would the volume be under a temperature of 21° C., pressure being neglected?

It is here required to ascertain what the volume of a gas, measured under standard conditions of temperature, would be at a given increased pressure, which by the law, will give an increased volume. Thus:

Reducing all temperatures to absolute

$$0^\circ \text{ C.} = 273^\circ \text{ C. absolute}$$

$$21^\circ \text{ C.} = 273 + 21 = 294^\circ \text{ C. absolute; then,}$$

$$273^\circ \text{ C.} : 294^\circ \text{ C.} :: 1.8 \text{ (liters)} : X \text{ (required volume)}$$

$$1.8 \times \frac{294}{273} = X; \text{ or, } X = 2 \text{ liters;}$$

that is, the volume at a temperature of 21° C., will be two liters.

As in the case of pressure, operations may be shortened by the following rule:

Multiply the volume actually measured by a fraction whose numerator and denominator will be absolute temperatures, the greater of which will be the denominator or numerator, according

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as whether the volume is to be decreased or increased, which may be seen by a simple inspection of the problem and understanding of Charles' law.

The application of the laws for both pressure and temperature may be combined in one operation. Taking the example:

A volume of ethylene, C_2H_4, measures two liters under a pressure of 750 millimeters of mercury and at a temperature of 21° C., what will be the volume under standard conditions of pressure and temperature?

Pressure measured under = 750 millimeters
Standard pressure = 760 millimeters
Temperature measured under = 21° C. = 273 + 21 = 294° C., absolute.
Standard temperature = 0° C. = 273° C.

As the pressure is to be increased, its effect will be to diminish the volume. As the temperature is to be decreased, its effect will be to diminish the volume also, consequently we have

$$2 \times \frac{750}{760} \times \frac{273}{294} = X; \text{ or, } X = 1.83 \text{ liters.}$$

Vapor Tension of Liquids. The pressure due to the tendency of volatile liquids to evaporate is termed vapor tension.

Vapor escapes from the surface of volatile liquids more or less readily at all temperatures, creating a pressure which varies with the temperature and is dependent upon the nature of the liquid. With the same liquid however, under like conditions of temperature, this pressure or vapor tension, as it is termed, remains constant.

With increase of temperature the vapor tension becomes greater, until it equals the external or atmospheric pressure, when what is termed boiling occurs—bubbles of vapor forming, and, in bursting, violently agitating the surface of the liquid.

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Vapor tension varies with the nature of the liquid; it is consequent then, that the temperatures at which *different* liquids boil will vary under like conditions of pressure.

The boiling point is defined above as the temperature at which the vapor tension becomes equal to the external pressure; it follows then, that as the external or atmospheric pressure varies, the boiling point also changes. With a decrease of the external pressure acting upon a

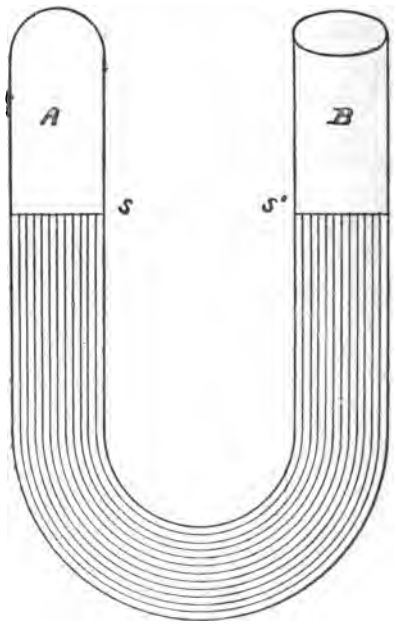

FIGURE 24.

liquid, the temperature of boiling is reduced, since the vapor tension need not become as high to equal the external pressure, and similarly with increased external pressure the boiling point is raised.

At the temperature of boiling the vapor tension equals

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the external pressure; this fact affords a ready means of determining the tension of different liquids, since it is but necessary to note the external pressure (by means of a barometer if atmospheric), and the temperature at which the liquid boils.

Effect of Vapor Tension on Volume. When a gas is measured over a liquid such as water or mercury, part of the gas volume may be vapor, dependent upon the temperature at which the measurement is made. To assist in separating the true gas volume from the liquid vapor, Table I has been compiled, since by previously determining the vapor tensions of the liquids employed for different temperatures, we may easily make corrections for the measured volumes. The accompanying illustration will serve to make this clear. It is desired to measure the volume of a gas, over water, in the closed arm A of the U tube, Figure 24. The water over which the measurement is made is at the same level as s and s' in both arms of the tube, indicating an external pressure equal to that within the closed arm. The pressure in the latter is, however, made up of both that exerted by the gas volume and that of the vapor tension. If we let

P_a = the atmospheric pressure in millimeters of mercury = the barometer reading,

P_t = the tension of water vapor at the temperature at which the measurement was made (found in Table I of vapor tensions),

P = the net or true pressure exerted by the gas to be measured.

Then,

P (true pressure) = P_a (atmospheric pressure) $- P_t$ (vapor tension).

Consequently, in taking account of the tension of vapor in the measurement of a gas volume, it is but necessary

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to find the true pressure (atmospheric less pressure due to vapor tension) for use in reducing to standard conditions.

The true or net pressure will, of course, always be less than atmospheric or that indicated by the barometer.

Let us consider the following example:

A volume of ethylene, C_2H_4, measured over water, under a pressure of 750 millimeters of mercury, and at a temperature of 21° C., gave a volume of 2 liters. What would its volume be under standard conditions of pressure and temperature, and when making correction for vapor tension?

We have:

Pressure measured under... = 750 mm. of mercury,
Standard pressure..... = 760 mm. of mercury,
From table, vapor tension of water at 21° C..... = 18.495 mm. of mercury,
Pressure corrected for vapor tension = 750 — 18.495... = 731.505 mm. of mercury,
Temp'ture measured under = 21° C., or 273 + 21... = 294° C., absolute,
Standard temp'ature = 0° C. = 273° C., absolute.

We have then:

$$2 \times \frac{750}{760} \times \frac{273}{294} = X, \text{ or } X = 1.83 \text{ liters}$$

as the volume when the pressure is uncorrected for vapor tension; and

$$2 \times \frac{731.505}{760} \times \frac{273}{294} = X, \text{ or } X = 1.78 \text{ liters}$$

as the volume when the pressure is corrected for vapor tension.

1.83 — 1.78 = 0.05 liters = the difference due to the presence of water vapor, which, had it not been taken into account, would have been considered as gas.

The foregoing tends to emphasize the necessity of making corrections for vapor tension where great accuracy is required in the measurement of gas volume.

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When a gas is measured over a liquid not easily volatile at ordinary temperatures, such as mercury, it may be saturated, previous to measurement, with water vapor by simply introducing a drop or so of water.

When the measurement is made over water, the gas will always be saturated. This is a necessary condition in order that use may be made of the tables of vapor tension, the tensions being known only for saturated gases.

In measuring perfectly dry gases over mercury at ordinary temperatures, no correction for vapor tension need be made, since the tension of vapor of mercury is but slight, and furthermore, is offset by a like tension of the mercury of the barometer at atmospheric pressures. It is but necessary in this case then, to simply make certain that both the barometer and gas volume being measured, are subject to like temperature and pressure, when the mercury of the barometer will stand lower on the scale by just the amount of the tension of mercury, due to the temperature acting on it, giving a reading therefore, equal to the true pressure to which the gas volume is subject.

In event of gases being measured over mercury at temperatures higher than the barometer is subject to, then the difference of vapor tension at the two temperatures (that of the barometer and that of the gas volume) should be subtracted from the atmospheric pressure to determine the true pressure.

The expansion of mercury at high temperatures must also be taken into account. The preferable method is, therefore, to keep the temperatures of both the gas volume (to be measured over mercury) and of the barometer the same whenever possible, thus obviating all necessity for correction for the tension or expansion of the mercury.

Table III gives the tension of mercury vapor at various temperatures.

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CHAPTER VII.

PROPERTIES OF GASES.—PREPARATION OF REAGENTS EMPLOYED.

Properties of gases. CARBON DIOXIDE. Synonyms: carbonic acid gas, choke-damp, after-damp, etc. Formula CO_2. Molecular mass (generally termed weight), 44; more correctly, according to atomic weights of Prof. F. W. Clarke, 39.002. Specific gravity compared to air, 1.5290. Weight of one liter, 1977 grams; weight of one cubic foot, 0.12343 pounds.

An irrespirable, colorless gas, denser than air, having a pungent odor and acid taste. It is fatal to animal life; extinguishes combustion. At standard conditions of temperature and pressure (0° C. and 760 millimeters of mercury) water absorbs or dissolves about one volume of carbon dioxide; as the pressure increases, temperature remaining constant, a greater absorption takes place, an additional volume being absorbed for each atmosphere of pressure added. Carbon dioxide becomes liquid at a pressure of 38.5 atmospheres and 0° C., with a specific gravity of 0.923. At −65° C. the liquid solidifies to a transparent mass like ice. A temperature of −140° C. may be obtained by means of frozen carbon dioxide moistened with ether and placed in a vacuum.

Preparation: Carbon dioxide may be prepared by the action of an acid upon some carbonate:

$$\underset{\text{Calcium Carbonate}}{CaCO_3} + \underset{\text{Nitric Acid}}{(HNO_3)_2} = \underset{\text{Calcium Nitrate}}{Ca(NO_3)_2} + \underset{\text{Water}}{H_2O} + \underset{\text{Carbon Dioxide}}{\uparrow CO_2}$$

ETHYLENE. Synonyms: olefiant gas, ethene, hydrogen di-carbide. Formula C_2H_4. Molecular mass, 28; according to Prof. F. W. Clarke, 27.9472. Specific gravity compared to air, 0.9847. Weight of one liter, 1.273 grams; weight of one cubic foot, 0.07949 pounds.

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An irrespiralbe, colorless gas, with odor of ether. Soluble in about eight times its volume of water. Combustible, emitting a brilliant white flame when burning in air, and evolving much smoke. Mixed in the proportion shown in formula below (one volume of ethylene to three volumes of oxygen), explodes violently on ignition. At 9.8 millimeters pressure, its evaporation produces a temperature of —150.4 degrees. It is the prlncipal constituent of the fixed illuminants or heavy hydrocarbons.

The reaction with oxygen is:

$$C_2H_4 + (O_2)_3 = (CO_2)_2 + (H_2O)_2$$

One volume of ethylene + three volumes of oxygen unite to form two volumes of carbon dioxide and two volumes of water, but the water may be considered as possessing no volume (owing to contraction in changing from a gaseous to liquid form), consequently the contraction due to the combustion of ethylene is $2C_2H_4$; 1 volume + 3 volumes = 4 volumes; 4—2 = 2 volumes contraction, or, for every volume of ethylene burned there is a resulting contraction of two times the volume of ethylene, or, contraction equals $2C_2H_4$. A reference to the reaction also shows that two volumes of carbon dioxide are formed for each volume of ethylene burned, or the carbon dioxide formed equals two times the ethylene burned; $CO_2 = 2C_2H_4$.

Preparation: Ethylene may be prepared by the action of sulphuric acid upon alcohol: $C_2H_6O = C_2\overset{\uparrow}{H}_4 + H_2O$.

Oxygen. Symbol O. Atomic mass, 16; or, according to Prof. F. W. Clarke, 15.9633. Valence II. Molecular mass, 32; or, according to the atomic weight of Prof. F. W. Clarke, 31.9266. Specific gravity compared to air, 1.1051. Weight of one liter, 1.4298 grams. Weight of one cubic foot, 0.08948 grams.

Oxygen is respirable when pure, accelerating the respiration; a colorless, odorless, tasteless gas, of greater

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density than air, and slightly soluble in water, 100 volumes of water at 0° C. taking up 4.1 volumes of oxygen. The union of any element with oxygen is what is generally implied by combustion. The action of oxygen in air is much less active in such union than when pure, owing to the dilution with nitrogen. Combustion with oxygen is attended with light and heat. Oxygen becomes liquid at 20 atmospheres of pressure, at a temperature of —136° C.

Preparation: Oxygen may be prepared by heating potassium chlorate, mixed with one-quarter of its weight of manganese dioxide:

$$\underset{\text{Potassium Chlorate}}{(K\,Cl\,O_3)_2} + \underset{\text{Manganese Dioxide}}{MnO_2} = \underset{\text{Potassium Chloride}}{(K\,Cl)_2} + \underset{\text{Manganese Dioxide Unchanged}}{MnO_2} + \underset{\text{Oxygen}}{\overset{\uparrow}{(O_2)_3}}$$

Carbon Monoxide. Synonyms: carbonic oxide, carbonyl. Formula, CO. Molecular mass, 28; according to Prof. F. W. Clarke, 27.9369. Specific gravity compared to air, 0.9674. Weight of one liter, 1.251 grams. Weight of one cubic foot, 0.07810 pounds.

It is an irrespirable, colorless gas, with suffocating odor. One per cent. in air proves fatal to life. Combustible, burning with a blue flame. It is a constituent of water gas, made by passing steam over incandescent fuel, and has, in this connection, been the topic of much discussion and even legislative interference, owing to the difficulty of detection and fatal effects on life. It is condensible to a liquid at —139.5° C., and 35.5 atmospheres.

The reaction with oxygen is $CO + (O_2)_{\frac{1}{2}} = CO_2$.

One volume of carbon monoxide combining with one-half volume of oxygen forms one volume of carbon dioxide; or, the contraction is $1\frac{1}{2} - 1 = \frac{1}{2}$ or $\frac{1}{2}CO$. The carbon dioxide formed equals the volume of carbon monoxide burned, or $CO_2 = 1CO$.

Preparation: Carbon monoxide may be prepared by heating oxalic acid with strong sulphuric acid:

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$$\underset{\text{Oxalic Acid}}{H_2C_2O_4} = \underset{\text{Water}}{H_2O} + \underset{\text{Carbon Dioxide}}{CO_2} + \underset{\text{Carbon Monoxide}}{\uparrow CO}$$

As seen, CO_2 is also present in the products, but can be removed by treating with potassium hydroxide, absorbing it as in gas analysis.

NITROGEN. Symbol N. Atomic mass, 14; according to Prof. F. W. Clarke, 14.01. Valence I, III and V. Molecular mass, 28; according to atomic mass of Prof. F. W. Clarke, 28.02. Specific gravity compared to air, 0.9714. Weight of one liter, 1.2561 grams; weight of one cubic foot, 0.07842 pounds.

Nitrogen is an irrespirable (it exerts no injurious action upon animal tissue, but does not support life), colorless, odorless, and tasteless gas of less density than air, slightly soluble in water, 2.5 volumes being absorbed by 100 of water. It is inert as regards combustion, uniting with oxygen only at an elevated temperature. Cooled to —150° C., in liquid ethylene, boiling under a pressure of 10 millimeters; nitrogen is liquefied by a pressure of about 30 atmospheres.

Preparation: Nitrogen may be prepared by heating ammonium nitrate:

$$\underset{\text{Ammonium Nitrate}}{(NH_4)\,NO_3} = \underset{\text{Water}}{(H_2O)_2} + \underset{\text{Nitrogen}}{\uparrow N_2}$$

HYDROGEN: Symbol, H; atomic mass, 1; Valence, I; molecular mass 2; specific gravity compared to air, 0.0695; weight of one liter, 0.089578 grams; weight of one cubic foot, 0.005592.

An irrespirable, colorless, odorless and tasteless gas, and the lightest form of matter known, being about 14.43 times lighter than air. It is slightly soluble in water, 1.9 volumes being absorbed by 100 volumes of water. Heated to about 500° C., it is combustible, combining with oxygen with evolutions of light and heat. It produces a pale,

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bluish flame, which becomes bright with increasing pressure. Hydrogen in burning evolves 34,462 calories per kilogram. Cooled in boiling nitrogen to $-213°$ C., under a pressure of 160 atmospheres, hydrogen has been brought to a colorless, transparent liquid.

The reaction with oxygen is:

$$H_2 + (O_2)_{\frac{1}{2}} = H_2O$$

One volume of hydrogen combining with one-half volume of oxygen forms water, the volume of the latter being neglected for reasons heretofore given; hence we have 1 volume + ½ volume, or 1½ volumes contracting to zero volumes; or, the amount of contraction equals 1½ volumes, which is 1½ times the amount of hydrogen burned. (1½H).

Preparation: Hydrogen may be prepared by the action of zinc upon an acid, as sulphuric acid:

$$\underset{\substack{\text{Hydrogen Sulphate or Sulphuric Acid}}}{H_2(SO_4)} + \underset{\text{Zinc}}{Zn} = \underset{\text{Zinc Sulphate}}{Zn(SO_4)} + \underset{\text{Free Hydrogen}}{\uparrow H_2}$$

METHANE: Synonyms, marsh gas, fire-damp, hydrogen carbide; formula, CH_4; molecular mass, 16; according to Prof. F. W. Clarke, 15.9736. Specific gravity compared to air, 0.5560; weight of one liter, 0.719 grams; weight of one cubic foot, 0.04488 pounds.

An irrespirable, colorless, odorless, tasteless gas, and is the next lightest gas to hydrogen. It is slightly soluble in water; combustible, emitting a pale, faintly-luminous flame when burning in air. Mixed with oxygen in the proportions expressed in the reaction below, two volumes of oxygen or about ten volumes of air, forms an explosive mixture, often the cause of serious accidents in coal mines, where it collects, together with other explosive gases.

The reaction with oxygen is:

$$CH_4 + (O_2)_2 = CO_2 + (H_2O)_2$$

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One volume of methane combining with two volumes of oxygen, forms one volume of carbon dioxide and water. The volume of water being neglected, we have 1 volume + 2 volumes, or 3 volumes contracting to 1 volume; or, the amount of contraction equals 2 volumes, which is 2 times the volume of methane burned. ($2CH_4$). Furthermore, for each volume of methane burned there is one volume of carbon dioxide formed, or, $CO_2 = CH_4$.

Preparation. Methane may be prepared by heating sodium acetate in presence of sodium hydroxide:

$$CO\begin{cases} CH_3 \\ ONa \end{cases} + \begin{matrix} Na \\ H \end{matrix}\Big\} O = CO\begin{cases} ONa \\ ONa \end{cases} + \uparrow CH_4$$

Sodium Acetate — Sodium Hydroxide — Sodium Carbonate — Methane

Preparation of the Reagents Employed. POTASSIUM HYDROXIDE. Dissolve 500 grams of commercial hydroxide (which has not been purified by alcohol) in one liter of pure water. It is ready for use as soon as made. Capacity: One cubic centimeter absorbs 40 cubic centimeters of carbon dioxide.

SODIUM HYDROXIDE. Make a saturated solution of the commercial hydroxide in pure water.

BARIUM HYDROXIDE. Make a saturated solution of barium oxide in water, (the barium oxide slakes).

Of these reagents, the first is preferable owing to its rapidity of action, the second to its cheapness, and the third to its accuracy where the carbon dioxide is in small quantities.

BROMINE WATER. Made by adding a little bromine to a liter of water, very little being required to saturate the water, causing it to give off bromine vapors.

POTASSIUM PYROGALLATE To 50 grams of pyrogallic acid add 1000 cubic centimeters of potassium hydroxide as made above. Keep well corked owing to its affinit

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for the oxygen of the air. It is ready for use as soon as made. Capacity: One cubic centimeter absorbs two cubic centimeters of oxygen.

CUPROUS CHLORIDE. Place in a liter reagent bottle 300 grams of copper oxide, and on this arrange a bunch of copper wire to reach the entire length of the bottle. Then fill with hydrochloric acid (specific gravity 1.10). The bottle is shaken, well corked to prevent the absorption of oxygen, and allowed to stand in the dark till perfectly clear, when it is ready for use. Exposure to light will cause it to assume a brownish color, which does not affect its action, however. Capacity: One cubic centimeter absorbs one cubic centimeter of carbon monoxide.

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TABLE I.

Tension of water vapor in millimeters of mercury for different temperatures. Also the weight in grams of the vapor contained in a cubic meter of air when saturated.

Degrees Centigrade	Tension in Millimeters	Weight in Grams	Degrees Centigrade	Tension in Millimeters	Weight in Grams	Degrees Centigrade	Tension in Millimeters	Weight in Grams
−20.	0.927		5.4	6.717		13.2	11.309	
−10.	2.093		5.6	6.810		13.4	11.456	
−2.	3.955		5.8	6.904		13.6	11.605	
−1.8	4.016		6.	6.998	7.3	13.8	11.757	
−1.6	4.078		6.2	7.095		14.	11.908	12.
−1.4	4.140		6.4	7.193		14.2	12.064	
−1.2	4.203		6.6	7.292		14.4	12.220	
−1.	4.267		6.8	7.392		14.6	12.378	
−0.8	4.331		7.	7.492	7.7	14.8	12.538	
−0.6	4.397		7.2	7.595		15.	12.699	12.8
−0.4	4.463		7.4	7.699		15.2	12.864	
−0.2	4.531		7.6	7.840		15.4	13.029	
0.	4.600		7.8	7.910		15.6	13.197	
+0.2	4.667		8.	8.017	8.1	15.8	13.366	
+0.4	4.733		8.2	8.126		16.	13.536	13.6
+0.6	4.801		8.4	8.236		16.2	13.710	
+0.8	4.871		8.6	8.347		16.4	13.885	
+1.	4.940		8.8	8.461		16.6	14.062	
+1.2	5.011		9.	8.574	8.8	16.8	14.241	
+1.4	5.082		9.2	8.690		17.	14.421	14.5
+1.6	5.155		9.4	8.807		17.2	14.605	
+1.8	5.228		9.6	8.925		17.4	14.790	
+2.	5.302		9.8	9.045		17.6	14.977	
+2.2	5.378		10.	9.165	9.4	17.8	15.167	
+2.4	5.454		10.2	9.288		18.	15.357	15.1
+2.6	5.530		10.4	9.412		18.2	15.552	
+2.8	5.608		10.6	9.537		18.4	15.747	
+3.	5.687		10.8	9.665		18.6	15.945	
+3.2	5.767		11.	9.792	10.	18.8	16.145	
+3.4	5.848		11.2	9.923		19.	16.346	16.2
+3.6	5.930		11.4	10.054		19.2	16.552	
3.8	6.014		11.6	10.187		19.4	16.758	
4.	6.097		11.8	10.322		19.6	16.967	
4.2	6.183		12.	10.457	10.6	19.8	17.179	
4.4	6.270		12.2	10.596		20.	17.391	17.2
4.6	6.350		12.4	10.734		20.2	17.608	
4.8	6.445		12.6	10.875		20.4	17.826	
5.	6.534	6.8	12.8	10.019		20.6	18.047	
5.2	6.625		13.	11.162	11.3	20.8	18.271	

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Tension of water vapor in millimeters of mercury for different temperatures. Also the weight in grams of the vapor contained in a cubic meter of air when saturated.

Degrees Centigrade	Tension in Millimeters	Weight in Grams	Degrees Centigrade	Tension in Millimeters	Weight in Grams	Degrees Centigrade	Tension in Millimeters	Weight in Grams
21.	18.495	18.2	27.6	27.455		99.3	741.16	
21.2	18.724		27.8	27.778		99.4	743.83	
21.4	18.954		28.	28.101	27.	99.5	746.5	
21.6	19.187		28.2	28.433		99.6	749.18	
21.8	19.423		28.4	28.765		99.7	751.87	
22.	19.659	19.3	28.6	29.101		99.8	754.57	
22.2	19.901		28.8	29.441		99.9	757.28	
22.4	20.143		29.	29.782	28.6	100.	760.	
22.6	20.389		29.2	30.131		100.1	762.73	
22.8	20.639		29.4	30.479		100.2	765.46	
23.	20.888	20.4	29.6	30.833		100.3	768.20	
23.2	21.144		29.8	31.190		100.4	771.95	
23.4	21.400		30.	31.548	29.2	100.5	773.71	
23.6	21.659		31.	33.405		100.6	776.48	
23.8	21.921		32.	35.359		100.7	779.26	
24.	22.184	21.5	33.	37.410		100.8	782.04	
24.2	22.453		34.	39.565		100.9	784.83	
24.4	22.723		35.	41.827		101.	787.63	
24.6	22.996		40.	54.906		105.	960.41	
24.8	23.273		45.	71.391		110.	1075.37	
25.	23.550	22.9	50.	91.982		120.	1491.28	
25.2	23.834		55.	117.478		130.	2030.28	
25.4	24.119		60.	148.791		140.	2717.63	
25.6	24.406		65.	186.945		150.	3581.23	
25.8	24.697		70.	233.093		160.	4651.62	
26.	24.988	24.2	75.	288.517		170.	5961.66	
26.2	25.288		80.	354.643		180.	7546.39	
26.4	25.588		85.	433.041		190.	9442.70	
26.6	25.891		90.	525.450		200.	11688.96	
26.8	26.198		95.	633.778		220.	17390.	
27.	26.505	25.6	99.	733.21		224.7	25 atmospheres	
27.2	26.820		99.1	735.85				
27.4	27.136		99.2	738.5				

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TABLE II.

FRENCH MEASURE.

One Millimetre ($\frac{1}{1000}$ of a metre)	0.039370 inches
One Centimetre ($\frac{1}{100}$ of a metre)	0.393704 inches
One Decimetre ($\frac{1}{10}$ of a metre)	3.937043 inches
One Metre (unit of length)	39.370432 inches
One Decametre (10 metres)	393.704320 inches
One Hectometre (100 metres)	3937.043196 inches
One Kilometre (1000 metres).	39370.431960 inches
One Myriametre (10,000 metres)	393704.319600 inches
or, 6 miles, 376 yards, 0 feet and $8\frac{8}{16}$ inches	

TABLE III.

TENSION OF MERCURY VAPOR.

Degrees Centi-grade	Tension in Millimetres	Degrees Centi-grade	Tension in Millimetres	Degrees Centi-grade	Tension in Millimetres
100	0.75	180	11.00	260	96.73
110	1.07	190	14.84	270	123.01
120	1.53	200	19.90	280	155.17
130	2.18	210	26 35	290	194.46
140	3.06	220	34.70	300	242.15
150	4.27	230	45.35	310	299.69
160	5.90	240	58.82	320	368.73
170	8.09	250	75.75	330	450.91

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INDEX.

Absorption pipette, manipulation of the, 54–56
After-damp, 84
Analysis of a gas, 12–16
coal gas, 35–38, 57–61
scheme for the, 67–72
Barium hydroxide, preparation of, 89
use of, as a reagent, 13
Benzene or benzene vapors, absorption of, 68
Boiling, definition of, 79
point, definition of, 80
Boyle's law, 75
Bromine water, 14
preparation of, 89
Burette, measuring, 9
to calibrate a, 9, 10
Carbon dioxide, absorption of, 68
with a reagent, 13
amount of, formed by the combustion of the gas residue, 37
determination of, 13, 14, 21, 22, 29, 30
percentage of in coal gas, 57, 58
properties and preparation of, 84
monoxide, absorbent for, 15
absorption of, 65, 66, 68, 69
determination of, 15, 16, 22, 31
percentage of, in coal gas, 36, 58
properties and preparation of, 86, 87
Carbonic acid gas, 84
oxide, 86, 87
Carbonyl, 86, 87
Charles' law, 77–79
Chimney gases, apparatus for, 7
examination of, by means of the Orsat apparatus, 17–23
Chloride, cuprous, 15
Choke damp, 84
Coal gas, analysis of, 35–38, 57–61
percentage of carbon dioxide in, 57, 58
monoxide in, 36, 58
heavy hydrocarbons in, 58
illuminants in, 35, 36
oxygen in, 36, 58
scheme for the analysis of, 67–72
Collection tubes, 1, 2
Compound pipettes, manipulation of, the, 57
Conduit, currents in a, 5, 6
Correction for pressure, temperature and vapor tension, 73–75
Cuprous chloride, 15
absorption method of making the, 68, 69
preparation of, 90
Double absorption pipette, 45
for solid and liquid reagents, 45–47
Dowson producer gas, partial analysis of, 15, 16
Elliott apparatus, 24–38
description of, 24–26
errors in the results obtained with the, 24
operation with the, 26–29
principal innovation with the, 24
table of analyses made with the, 38
Ethene, 84, 85
Ethylene, 14
absorbent for, 14
pipette, 48
properties and preparation of, 84, 85
Explosion pipette, 49, 50
with electrodes for the decomposition of water, 52, 53
Fire damp, 88, 89
Fisher's modification of the Orsat apparatus, 18, 19
Flue, currents in a, 5, 6
gas, analysis of, 38
Fractional combustion of hydrogen, 61–66
French measures, table of, 93
Furnace gases, apparatus for, 7
examination of, by means of the Orsat apparatus, 17–23
piping for running into the, 5
Gas, analysis of a 12–16
technical, 7–16
apparatus for, 7
apparatus for obtaining a rough estimate of the constituents of a, 7–11
collection of samples of, 1–6
composition, alteration of the, by iron piping raised to a temperature of redness, 5

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